



A TEXT-BOOK OF  
INORGANIC CHEMISTRY.  
VOLUME VII. PART III.



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# A TEXT-BOOK OF INORGANIC CHEMISTRY.

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EDITED BY  
J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,  
CARNEGIE GOLD MEDALLIST.

## VOLUME VII. PART III.

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### CHROMIUM AND ITS CONGENERS.

BY  
REECE H. VALLANCE, AND ARTHUR A. ELDRIDGE,  
M.Sc. (BHAM.), A.I.C. B.Sc. (LOND.), F.I.C.

With Frontispiece and Illustrations.

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## GENERAL INTRODUCTION TO THE SERIES.

DURING the past few years the civilized world has begun to realize the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group 0, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasize their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are sub-

jects of supreme importance to the student of Inorganic Chemistry and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II, along with the Elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV, along with the Elements of Group III, as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II and V respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II under ammonium, and in Volume IX under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicles and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing in the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

Hydrogen	=	1.00762.	Oxygen	=	16.000.
Sodium	=	22.996.	Sulphur	=	32.065.
Potassium	=	39.100.	Fluorine	=	19.015.
Silver	=	107.880.	Chlorine	=	35.457.
Carbon	=	12.008.	Bromine	=	79.916.
Nitrogen	=	14.008.	Iodine	=	126.920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive,

as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xv-xvii.

The addition of the *Table of Dates of Issue of Journals* (pp. xix-xxvi) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin and Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

August 1920.





## PREFACE.

THIS volume is devoted to the four elements : chromium, molybdenum, tungsten, and uranium. The study of each of these provides much that is fascinating to the chemist, and much that calls for elucidation and further research. The growing importance of the metals and their compounds in industry, especially in the manufacture of steels and special alloys, and in the production of glazes and pigments, emphasises their claims to interest. The use of tungsten in electrical work is continually finding wider application.

The types of compounds produced by the elements of the chromium group are of greater variety than is usual, owing to the varying degrees of combining power exhibited, and the fact that the elements function both in electropositive and electronegative radicals. Moreover, in many cases the types of compounds are of considerable complexity, as seen in the large classes of heteropoly-compounds produced, particularly by molybdenum and tungsten. The decorative tungsten bronzes are of exceptional interest.

Uranium is unique as the element of highest atomic weight, and the terminal member of the periodic system. It was in a compound of this element that radioactive phenomena were first recognised, and now, as by-products in the extraction of radium, uranium compounds are produced in considerable quantity. It remains, however, for the chemist to show how this material can be utilised more extensively in the arts or in industry.

All the more important inorganic salts of the elements, whether the metal occurs in the basic or the acidic radical, are described in the present work. Atomic weights have been recalculated from the original experimental data on the basis indicated in the General Introduction. Every effort has been made to render accurate and reliable the many references supporting the text, and it is hoped that the entire work will merit the confidence of all who consult it. The Authors will be grateful for any criticisms and suggestions for improvement.

The Authors desire to thank the Editor, Dr J. Newton Friend, who has read through the whole of the manuscript and proof, for the kindly help and advice which he has so readily placed at their disposal.

REECE H. VALLANCE.  
ARTHUR A. ELDRIDGE.

*August 1920.*



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# LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

ABBREVIATED TITLE.	JOURNAL.
<i>Afhandl. Fys. Kem.</i> . . .	Afhandlingar i Fysik, Kemi och Mineralogi.
<i>Amer. Chem. J.</i> . . .	American Chemical Journal.
<i>Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . .	The Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim.</i> . . .	Annales de Chimie (1719-1815, and 1914 +).
<i>Ann. Chim. anal.</i> . . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
<i>Ann. Chim. Phys.</i> . . .	Annales de Chimie et de Physique (Paris) (1816-1913).
<i>Ann. Mines</i> . . .	Annales des Mines.
<i>Ann. Pharm.</i> . . .	Annalen der Pharmacie (1832-1839).
<i>Ann. Phys. Chem.</i> . . .	Annalen der Physik und Chemie (1819-1899).
<i>Ann. Physik</i> . . .	Annalen der Physik (1799-1818, and 1900 +).
<i>Ann. Physik, Beibl.</i> . . .	Annalen der Physik, Beiblätter.
<i>Ann. Sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.
<i>Arbeiten Kaiserl. Gesundheitsamte</i> . . .	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
<i>Arch. exp. Pathol. Pharmac.</i> . . .	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i> . . .	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i> . . .	Archives des Sciences physiques et naturelles, Genève.
<i>Atti Acc. Torino</i> . . .	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i> . . .	Atti della Reale Accademia Lincei.
<i>B.A. Reports</i> . . .	British Association Reports.
<i>Ber.</i> . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Akad. Ber.</i> . . .	Ses Sitzungsber. K. Akad. Wiss. Berlin
<i>Ber. Deut. physikal. Ges.</i> . . .	Berichte der Deutschen physikalischen Gesellschaft.
<i>Bot. Zeit.</i> . . .	Botanische Zeitung.
<i>Bull. Acad. Sci. Cracow</i> . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. roy. Belg.</i> . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. de Belg.</i> . . .	Bulletin de la Société chimique Belgique.
<i>Bull. Soc. chim.</i> . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. franc. Min.</i> . . .	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. min. de France</i> . . .	Bulletin de la Société minéralogique de France.
<i>Bull. U.S. Geol. Survey</i> . . .	Bulletins of the United States Geological Survey.
<i>Centr. Min.</i> . . .	Centralblatt für Mineralogie.
<i>Chem. Ind.</i> . . .	Die Chemische Industrie.
<i>Chem. News</i> . . .	Chemical News.
<i>Chem. Weekblad.</i> . . .	Chemisch Weekblad.
<i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.
<i>Chem. Zeit.</i> . . .	Chemiker Zeitung (Cöthen).
<i>Compt. rend.</i> . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
<i>Crell's Annalen</i> . . .	Chemische Annalen für die Freunde der Naturlehre, von L. Crell.
<i>Dingl. poly. J.</i> . . .	Dingler's polytechnisches Journal.
<i>Drude's Annalen</i> . . .	Annalen der Physik (1900-1906).
<i>Electroch. Met. Ind.</i> . . .	Electrochemical and Metallurgical Industry.

ABBREVIATED TITLE.	JOURNAL.
<i>Eng. and Min. J.</i>	Engineering and Mining Journal.
<i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Gehlen's Allg. J. Chem.</i>	Allgemeines Journal der Chemie.
<i>Gilbert's Annalen</i>	Annalen der Physik (1799-1824).
<i>Giorn. di Scienze Naturali ed Econ.</i>	Giornale di Scienze Naturali ed Economiche.
<i>Geol. Mag.</i>	Geological Magazine.
<i>Int. Zeitsch. Metallographie</i>	Internationale Zeitschrift für Metallographie.
<i>Jahrb. kk. geol. Reichsanst.</i>	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
<i>Jahrb. Miner.</i>	Jahrbuch für Mineralogie.
<i>Jahresber.</i>	Jahresbericht über die Fortschritte der Chemie.
<i>Jenaische Zeitsch.</i>	Jenaische Zeitschrift für Naturwissenschaft.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Chem. Soc.</i>	Journal of the Chemical Society.
<i>J. Chim. phys.</i>	Journal de Chimie physique.
<i>J. Gasbeleuchtung</i>	Journal für Gasbeleuchtung.
<i>J. Geology</i>	Journal of Geology.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Metals</i>	Journal of the Institute of Metals.
<i>J. Miner. Soc.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i>	Journal of Physical Chemistry.
<i>J. Physique</i>	Journal de Physique.
<i>J. prakt. Chem.</i>	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia (Petrograd).
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>Landw. Jahrb.</i>	Landwirtschaftliche Jahrbücher.
<i>Mém. Paris Acad.</i>	Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France.
<i>Mon. scient.</i>	Moniteur scientifique.
<i>Monatsh.</i>	Monatshäfte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Münch. Med. Wochenschr.</i>	Münchener Medizinische Wochenschrift.
<i>Nature</i>	Nature.
<i>Nuovo Cim.</i>	Il nuovo Cimento.
<i>Öfvers. K. Vet.-Akad. Forh.</i>	Öfversigt af Kongliga Vetenskaps-Akademien's Förhandlingar.
<i>Oesterr. Chem. Zeit.</i>	Oesterreichische Chemiker-Zeitung.
<i>Pflüger's Archiv.</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Centralhalle.
<i>Pharm. Post</i>	Pharmazeutische Post.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh, and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Phys. Review</i>	Physical Review.
<i>Physikal. Zeitsch.</i>	Physikalische Zeitschrift.
<i>Pogg. Annalen</i>	Poggendorff's Annalen der Physik und Chemie (1824-1877).
<i>Proc. Chem. Soc.</i>	Proceedings of the Chemical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i>	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
<i>Proc. Roy. Irish Acad.</i>	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Phil. Soc. Glasgow</i>	Proceedings of the Royal Philosophical Society of Glasgow.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society of London.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Rec. Trav. chim.</i>	Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
<i>Roy. Inst. Reports</i>	Reports of the Royal Institution.
<i>Schweigger's J.</i>	Journal für Chemie und Physik.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.

ABBREVIATED TITLE.	JOURNAL.
<i>Sitzungsber. K. Akad. Wiss. Wien.</i>	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
<i>Sci. Proc. Roy. Dubl. Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Techn. Jahresber.</i>	Jahresbericht über die Leistungen der Chemischen Technologie.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society.
<i>Trans. Chem. Soc.</i>	Transactions of the Chemical Society.
<i>Trans. Inst. Min. Eng.</i>	Transactions of the Institution of Mining Engineers.
<i>Trav. et Mém. du Bureau intern. des Poids et Mes.</i>	Travaux et Mémoires du Bureau International des Poids et Mesures.
<i>Verh. Ges. deut. Naturforsch. Aerzte.</i>	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Wied. Annalen.</i>	Wiedemann's Annalen der Physik und Chemie (1877-1899).
<i>Wissenschaftl. Abhandl. phys.-tech. Reichsanst.</i>	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Chem.</i>	Kritische Zeitschrift für Chemie.
<i>Zeitsch. Chem. Ind. Kolloide.</i>	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
<i>Zeitsch. Elektrochem.</i>	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i>	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. Nahr. Genuss-m.</i>	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. wiss. Photochem.</i>	Zeitschrift für wissenschaftliche Photographie, Photo-physik, und Photochemie.





# TABLE OF DATES OF ISSUE OF JOURNALS.

FOR the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer. J. Sci.	Ann. Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32-35	...	...	...	4-6	...	5-8	90	...
1	...	36-39	...	...	...	7-9	...	8-11	91	...
2	...	40-43	...	...	...	10-12	...	11-14	92	...
3	...	44-47	...	...	...	13-15	...	14-17	93	...
4	...	48-51	...	...	...	16-18	...	17-20	94	...
1805	...	52-55	...	...	...	19-21	...	20-23	95	...
6	...	56-60	...	...	...	22-24	...	23-26	96	...
7	...	61-64	...	...	...	25-27	...	26-29	97	...
8	...	65-68	...	...	...	28-30	...	29-32	98	...
9	...	69-72	...	...	...	31-33	(1) 1*	33, 34	99	...
1810	...	73-76	...	...	...	34-36	2	35, 36	100	...
11	...	77-80	...	...	...	37-39	3	37, 38	101	...
12	...	81-84	...	...	...	40-42	4	39, 40	102	...
13	...	85-88	...	...	...	43-46	6	41, 42	103	...
14	...	89-92	...	...	...	46-48	6	43, 44	104	...
1815	...	93-96	...	...	...	49-51	(2) 1	45, 46	105	...
16	...	(2) 1-3	...	...	...	52-54	2	47, 48	106	...
17	...	4-6	1, 2	...	...	55-57	3	49, 50	107	...
18	...	7-9	3	...	...	58-60	4	51, 52	108	...
19	(1) 1	10-12	4	...	...	61-63	5	53, 54	109	...
1820	2	13-15	5	...	1-3	64-66	6	55, 56	110	...
21	3	16-18	6	...	4-6	67-69	7	57, 58	111	...
22	4, 5	19-21	7	1, 2	7-9	70-72	8	59, 60	112	...
23	6	22-24	8	3-6	10-12	73-75	9	61, 62	113	...
24	7, 8	25-27	9	7-10	13-15	76	10	63, 64	114	1, 2
1825	9	28-30	10, 11	11-14	16-18	...	11	65, 66	115	3-5
26	10, 11	31-33	12, 13	15-19	19-22	...	12	67, 68	116	6-8
27	12	34-36	(2) 1, 2	20-23	23-26	Continued as Pogg. Annalen.	13	(2) 1, 2	117	9-11
28	13, 14	37-39	3, 4	24-26	27-30	...	14	3, 4	118	12-14
29	15, 16	40-42	5, 6	27-30	31-34	...	15	5, 6	119	15-17

\* First series known as *Bulletin de Pharmacie*.

Year.	Amer. J. Sci.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon. scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	...	...	...	...	35-38	16	...	...	7, 8	120	18-20	...	...	...
31	19, 20	...	7-8	31-34	...	...	39-42	17	...	...	9, 10	121	21-23	...	...	...
32	21, 22	1-4	(3) 1, 2	35-39	...	...	43-47	18	...	...	11 (3) 1	122	24-26	1	...	...
33	23, 24	5-8	3, 4	40-43	...	...	48-50	19	...	...	4, 5	123	27-30	2	...	...
34	25-27	9-12	5, 6	48-50	...	...	51-54	20	1-3	...	4, 5	124	31-33	...	...	...
1835	28, 29	13-16	7, 8	(2) 1-4	...	1	55-58	21	4-6	...	6, 7	125	34-36	...	...	...
36	30, 31	17-20	9, 10	5-8	...	2, 3	59-62	22	7-9	...	8, 9	126	37-39	...	...	...
37	32, 33	21-24	11, 12	9-12	...	4, 5	63-66	23	10-12	...	10, 11	127	40-42	...	...	...
38	34, 35	25-28	13, 14	13-16	...	6, 7	67-70	24	13-15	...	12, 13	128	43-45	3	...	...
39	36, 37	29-32	15, 16	17-20	...	8, 9	71-74	25	16-18	...	14, 15	129	46-48	...	...	...
1840	38, 39	33-36	73-75	...	...	10, 11	75-78	26	19-21	...	16, 17	130	49-51	...	...	...
41	40, 41	37-40	(3) 1-3	21-24	...	12, 13	79-82	27	22-24	...	18, 19	131	52-54	...	...	...
42	42, 43	41-44	4-6	25-28	...	14, 15	83-86	(3) 1, 2	25-27	...	20, 21	132	55-57	...	...	...
43	44, 45	45-48	7-9	33-36	...	16, 17	87-90	3, 4	28-30	...	22, 23	133	58-60	4	...	...
44	46, 47	49-52	5, 6	37-40	...	18, 19	91-94	5, 6	31-33	...	24, 25	134	61-63	...	...	...
1845	48-50	53-56	13-15	...	...	20, 21	95-98	7, 8	34-36	...	26, 27	135	64-66	...	...	...
46	(2) 1, 2	57-60	16-18	41-44	...	22, 23	99-102	9, 10	37-39	...	28, 29	136	67-69	...	...	...
47	3, 4	61-64	19-21	45-48	...	24, 25	103-106	11, 12	40-42	...	30, 31	137	70-72	...	...	...
48	5, 6	65-68	22-24	53-56	...	26, 27	107-110	13, 14	43-45	...	32, 33	138	73-75	1	...	...
49	7, 8	69-72	25-27	57-60	...	28, 29	111-114	15, 16	46-48	...	34, 35	139	76-78	2, 3	...	...
1850	9, 10	73-76	28-30	...	...	30, 31	115-118	17, 18	49-51	...	36, 37	140	79-81	3	...	...
51	11, 12	77-80	31-33	61-64	...	32, 33	119-122	19, 20	52-54	...	(4) 1, 2	141	82-84	4, 5	...	...
52	13, 14	81-84	34-36	65-68	...	34, 35	123-126	21, 22	55-57	...	3, 4	142	85-87	5	...	...
53	15, 16	85-88	37-39	73-76	...	36, 37	127-130	23, 24	58-60	...	5, 6	143	88-90	6	...	...
54	17, 18	89-92	40-42	77-80	...	38, 39	131-134	25, 26	61-63	...	7, 8	144	91-93	7	...	...
1855	19, 22	93-96	43-45	...	...	40, 41	135-138	27, 28	64-66	...	9, 10	145	94-96	8	...	...
56	21, 22	97-100	46-48	85-88	...	42, 43	139-142	29, 30	67-69	...	11, 12	146	97-99	9	...	...
57	23, 24	101-104	49-51	...	...	44, 45	143-146	31, 32	(1) 1	...	13, 14	147	100-102	10	...	...
58	25, 26	105-108	52-54	93-96	1	46, 47	147-150	33, 34	73-75	2	15, 16	148	103-105	11	...	...
59	27, 28	109-112	55-57	97-100	1	48, 49	151-154	35, 36	76-78	2	17, 18	149	106-108	12	...	...

\* Often referred to by Series: Series 3, vols. 1-16, 1871-1886; Series 4, vols. 1-24, 1887-1910; Series 5, vols. 1-9, 1911-1919 (one vol. yearly).

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Zeit.
1860	...	29, 30	...	113-116	...	58-60	17, 18	101-104	...	2	1, 2	...	...
61	...	31, 32	...	117-120	1	61-63	19, 20	105-108	...	3	3, 4	...	...
62	...	33, 34	...	121-124	2	64-66	(6) 1, 2	109-112	...	4	5, 6	...	...
63	...	35, 36	...	125-128	2	67-69	3, 4	113-116	...	5	7, 8	...	...
64	...	37, 38	...	129-132	3	(4) 1-3	5, 6	117-120	...	(2) 1, 2	9, 10	...	...
1865	...	39, 40	...	133-136	3, 4	4-6	7, 8	121-124	...	3, 4	11, 12	...	...
66	...	41, 42	...	137-140	4	7-9	9, 10	125-128	...	5, 6	13, 14	...	...
67	...	43, 44	...	141-144	5	10-12	11, 12	129-132	...	7, 8	15, 16	...	...
68	...	45, 46	...	145-148	6	13-15	13, 14	133-136	...	9, 10	17, 18	...	...
69	...	47, 48	...	149-152	...	16-18	15, 16	137-140	...	11, 12	19, 20	...	...
1870	...	49, 50	...	153-156	7	19-21	17, 18	141-144	...	13, 14	21, 22	...	...
71	...	(3) 1, 2	...	157-160	...	22-24	19, 20	145-148	...	15, 16	23, 24	...	...
72	...	3, 4	...	161-164	8	25-27	(7) 1, 2	149-150, 201*	...	17, 18	25, 26	...	...
73	...	5, 6	...	165-170	...	28-30	3, 4	201-203	...	19, 20	27, 28	...	...
74	...	7, 8	...	171-174	...	(5) 1-3	5, 6	204, 205	...	21, 22	29, 30	...	...
1875	...	9, 10	...	175-179	...	4-6	7, 8	206, 207	...	23, 24	31, 32	...	...
76	...	11, 12	...	180-183	...	7-9	9, 10	208, 209	...	25, 26	33, 34	...	...
77	...	13, 14	...	184-189	...	10-12	11, 12	210, 211	...	27, 28	35, 36	...	...
78	...	15, 16	...	190-194	...	13-15	13, 14	212, 213	...	29, 30	37, 38	...	...
79	...	17, 18	...	195-199	...	16-18	15, 16	214, 215	...	31, 32	39, 40	...	...
1880	...	19, 20	...	200-205	...	19-21	17, 18	216, 217	...	33, 34	41, 42	...	...
81	...	21, 22	...	206-210	...	22-24	19, 20	218, 219	...	35, 36	43, 44	...	...
82	...	23, 24	...	211-215	...	25-27	(8) 1, 2	220	...	37, 38	45, 46	...	...
83	...	25, 26	...	216-221	...	28-30	3, 4	221	...	39, 40	47, 48	...	...
84	...	27, 28	...	222-226	...	(6) 1-3	5, 6	222	...	41, 42	49, 50	...	...
1885	...	29, 30	...	227-231	...	4-6	7, 8	223	...	43, 44	51, 52	...	...
86	...	31, 32	...	232-236	...	7-9	9, 10	224	...	45, 46	53, 54	...	...
87	...	33, 34	...	237-242	...	10-12	11, 12	225	...	47, 48	55, 56	...	...
88	...	35, 36	...	243-249	...	13-15	13, 14	226	...	49, 50	57, 58	...	...
89	...	37, 38	...	250-255	...	16-18	15, 16	227	...	(3) 1, 2	59, 60	...	...

\* Joining Series 1 and 2 together. Also written as (3) 1, 2, 3, etc.

Year.	Compt. rend.	Dingl. poly. J.	Gazette.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Pharm. Chim.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh. scient.*	Nature.	Phil. Mag.
1860	50, 51	155-158	...	...	...	37, 38	79-81	...	...	4	...	19, 20
61	52, 53	159-162	...	...	...	39, 40	82-84	...	...	...	...	21, 22
62	54, 55	163-166	...	...	15	41, 42	85-87	...	...	...	...	23, 24
63	56, 57	167-170	...	...	16	43, 44	88-90	...	...	5	...	25, 26
64	58, 59	171-174	...	...	17	45, 46	91-93	...	...	6	...	27, 28
1865	60, 61	175-178	...	...	18	(4) 1, 2	94-96	...	...	7	...	29, 30
66	62, 63	179-182	...	...	19	3, 4	97-99	...	...	8	...	31, 32
67	64, 65	183-186	...	...	20	5, 6	100-102	...	...	9	...	33, 34
68	66, 67	187-190	...	...	21	7, 8	103-105	...	...	10	...	35, 36
69	68, 69	191-194	...	...	22	9, 10	106-108	1	...	11	1	37, 38
1870	70, 71	195-198	...	...	23	11, 12	(2) 1, 2	2	...	12	1, 2, 3	39, 40
71	72, 73	199-202	1	...	24	13, 14	3, 4	3	...	13	3, 4, 5	41, 42
72	74, 75	203-206	2	...	25	15, 16	5, 6	4	...	14	5, 6, 7	43, 44
73	76, 77	207-210	3	...	26	17, 18	7, 8	5	...	15	7, 8, 9	45, 46
74	78, 79	211-214	4	...	27	19, 20	9, 10	6	...	16	9, 10, 11	47, 48
1875	80, 81	215-218	5	...	28	21, 22	11, 12	7	...	17	11, 12, 13	49, 50
76	82, 83	219-222	6	...	29, 30	23, 24	13, 14	8	...	18	13, 14, 15	(5) 1, 2
77	84, 85	223-226	7	...	31, 32	25, 26	15, 16	9	...	19	15, 16, 17	3, 4
78	86, 87	227-230	8	...	33, 34	27, 28	17, 18	10	...	20	17, 18, 19	5, 6
79	88, 89	231-234	9	1	35, 36	29, 30	19, 20	11	...	21	19, 20, 21	7, 8
1880	90, 91	235-238	10	2	37, 38	(6) 1, 2	21, 22	12	...	22	21, 22, 23	9, 10
81	92, 93	239-242	11	3	39, 40	3, 4	23, 24	13	...	23	23, 24, 25	11, 12
82	94, 95	243-246	12	4	41, 42	5, 6	25, 26	14	1	24	25, 26, 27	13, 14
83	96, 97	247-250	13	5	43, 44	7, 8	27, 28	15	2	25	27, 28, 29	15, 16
84	98, 99	251-254	14	6	45, 46	9, 10	29, 30	16	3	26	29, 30, 31	17, 18
1885	100, 101	255-258	15	7	47, 48	11, 12	31, 32	17	4	27	31, 32, 33	19, 20
86	102, 103	259-262	16	8	49, 50	13, 14	33, 34	18	5	28	33, 34, 35	21, 22
87	104, 105	263-266	17	9	51, 52	15, 16	35, 36	19	6	29, 30	35, 36, 37	23, 24
88	106, 107	267-270	18	10	53, 54	17, 18	37, 38	20	7	31, 32	37, 38, 39	25, 26
89	108, 109	271-274	19	11	55, 56	19, 20	39, 40	21	8	33, 34	39, 40, 41	27, 28

\* See footnote, p. xi.

Year.	Phil. Trans.	Pogg. Annalen.	Proc. Chem. Soc.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. kryst. Min.	Zeitsch. physikal. Chem.
1860	150	109-111	...	10, 11	13	...	39-42	...	...	...	...	...	...
61	151	112-114	...	11	14	...	43, 44	...	...	...	...	...	...
62	152	115-117	...	11, 12	Continued	...	45, 46	...	...	1	...	...	...
63	153	118-120	...	12, 13	as J.	...	47, 48	...	...	2	...	...	...
64	154	121-123	...	13	Chem. Soc.	...	49, 50	...	...	3	...	...	...
1865	155	124-126	...	14	...	...	51, 52	...	...	4	...	...	...
65	156	127-129	...	15	...	...	53, 54	...	...	5	...	...	...
67	157	130-132	...	15, 16	...	...	55, 56	...	...	6	...	...	...
68	158	133-135	...	16, 17	...	...	57, 58	...	...	7	...	...	...
69	159	136-138	...	17, 18	...	...	59, 60	...	...	8	...	...	...
1870	160	139-141	...	18, 19	...	...	61, 62	...	...	9	...	...	...
71	161	142-144	...	19, 20	...	...	63, 64	...	...	10	...	...	...
72	162	145-147	...	20, 21	...	...	65, 66	...	...	11	...	...	...
73	163	148-150	...	21, 22	...	...	67, 68	...	...	12	...	...	...
74	164	151-153	...	22, 23	...	...	69, 70	...	...	13	...	...	...
1875	165	154-156	...	23, 24	...	...	71, 72	...	...	14	...	...	...
76	166	157-159	...	24, 25	...	...	73, 74	...	...	15	...	...	...
77	167	160	...	25, 26	...	...	75, 76	...	1, 2	16	...	1, 2	...
78	168, 169	Continued	...	26, 27	...	...	77, 78	...	3-5	17	...	2, 3	...
79	170	as Wied. Annalen.	...	27, 28	...	...	79, 80	...	6-8	18	...	3, 4	...
1880	171	...	...	28, 29, 30	...	...	81, 82	...	9-11	19	...	4, 5	...
81	172	...	...	30, 31	...	...	83, 84	...	12-14	20	...	5, 6	...
82	173	...	...	31, 32, 33	...	...	85, 86	...	15-17	21	...	6, 7	...
83	174	...	...	33, 34	...	1	87, 88	...	18-20	22	...	7, 8	...
84	175	...	...	34, 35, 36	...	2	89, 90	...	21-23	23	...	8, 9, 10	...
1885	176	...	...	36, 37, 38	...	3	91, 92	...	24-26	24	...	10, 11	...
86	177	...	1	38, 39	...	4	93, 94	...	27-29	25	...	11, 12	...
87	A. 178	...	2	40, 41	...	5	95, 96	...	30-32	26	...	12, 13	...
88	179	...	3	42, 43	...	6	97	...	33-35	27	...	13, 14, 15	...
89	180	...	4	43, 44, 45	...	7	98	...	36-38	28	...	15	...
		...	5	45, 46, 47	...	8		...			...		2, 4
		...			...			...			...		3, 4

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Weekblad.	Chem. Zeit.	Compt. rend.
1890	12	39, 40	15	256-260	19-21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
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92	14	43, 44	17	267-271	25-27	(9) 1, 2	230	25	7, 8	65, 66	10, 11	...	16	114, 115
93	15	45, 46	18	272-277	28-30	3, 4	231	26	9, 10	67, 68	12, 13	...	17	116, 117
94	16	47, 48	19	278-283	(7) 1-3	5, 6	232	27	11, 12	69, 70	14, 15	...	18	118, 119
1895	17	49, 50	20	284-288	4-6	7, 8	233	28	13, 14	71, 72	16, 17	...	19	120, 121
96	18	(4) 1, 2	21	289-293	7-9	9, 10	234	29	15, 16	73, 74	18, 19	...	20	122, 123
97	19	3, 4	22	294-298	10-12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299-303	13-15	13, 14	236	31	19, 20	77, 78	22, 23	...	22	126, 127
99	21, 22	7, 8	24	304-309	16-18	15, 16	237	32	21, 22	79, 80	24, 25	...	23	128, 129
1900	23, 24	9, 10	25	310-313	19-21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
01	25, 26	11, 12	26	314-319	22-24	19, 20	239	34	25, 26	83, 84	28, 29	...	25	132, 133
02	27, 28	13, 14	27	320-325	25-27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	...	26	134, 135
03	29, 30	15, 16	28	326-329	28-30	3, 4	241	36	29, 30	87, 88	32, 33	...	27	136, 137
04	31, 32	17, 18	29	330-337	(8) 1-3	5, 6	242	37	31, 32	89, 90	34, 35	...	28	138, 139
1905	33, 34	19, 20	30	338-343	4-6	7, 8	243	38	33, 34	91, 92	36, 37	...	29	140, 141
06	35, 36	21, 22	31	344-350	7-9	9, 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
07	37, 38	23, 24	32	351-357	10-12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	...	31	144, 145
08	39, 40	25, 26	33	358-363	13-15	13, 14	246	41	3, 4	97, 98	42, 43	5	32	146, 147
09	41, 42	27, 28	34	364-371	16-18	15, 16	247	42	5, 6	99, 100	44, 45	6	33	148, 149
1910	43, 44	29, 30	35	372-377	19-21	17, 18	248	43	7, 8	101, 102	46, 47	7	34	150, 151
11	45, 46	31, 32	36	378-385	22-24	19, 20	249	44	9, 10	103, 104	48, 49	8	35	152, 153
12	47, 48	33, 34	37	386-394	25-27	(11) 1, 2	250	45	11, 12	105, 106	50, 51	9	36	154, 155
13	49, 50	35, 36	38	395-401	28-30	3, 4	251	46	13, 14	107, 108	52, 53	10	37	156, 157
14	Publication	37, 38	39	...	...	5, 6	252	47	15, 16	109, 110	54, 55	11	38	158, 159
1915	ceased	39, 40	40	...	...	...	253	48	17, 18	111, 112	56, 57	12	39	160, 161
16	...	41, 42	41	...	...	...	254	49	19, 20	113, 114	58, 59	13	40	162, 163
17	...	43, 44	42	...	...	...	255	50	21, 22	115, 116	60, 61	14	41	164, 165
18	...	45, 46	43	...	...	...	...	51	23, 24	117, ...	62, 63	15	42	166, 167
19	...	47, 48	44	...	...	...	...	59	25, 26	...	...	...	...	...

Year.	Dingl. poly. J.	Gazette.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon. * scient.	Nature.	Phil. Mag.
1890	275-278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279-282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283-286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287-290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291-294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295-298	25	17	67, 68	...	(6) 1, 2	...	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299-302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303-306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307-310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311-314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
01	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
02	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
03	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
04	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
06	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
07	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
08	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
09	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79, 82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82-85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85-88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89, 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100-102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102-104	37, 38

\* See footnote, p. xi.



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1890	A. 181	...	6	47, 48, 49	9	99	10	39-41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42-44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45-47	31	5	1, 2	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48-50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51-53	33	7	5-7	1	23, 24	13-15
1895	186	...	11	57, 58, 59	14	104	15	54-56	34	8	8-10	1, 2	24, 25	16-18
96	187, 188	...	12	59, 60	15	105	16	57-59	35	9	11, 12, 13	2, 3	26-28	19-21
97	189, 190	...	13	60, 61, 62	16	106	17	60-63	36	10	13-15	3, 4	28, 29	22-24
98	191	...	14	62, 63, 64	17	107	18	64-66	37	11	16-19	4, 5	29-31	25-27
99	192, 193	...	15	64, 65, 66	18	108	19	67-69	38	12	19-22	5, 6	31, 32	28-31
1900	194, 195	1	16	66, 67	19	109	20	Con- tinued as	39	13	22-25	6, 7	32-34	32-35
01	196, 197	2	17	68, 69	20	110	21	Annalen	40	14	26-29	7	34-36	36-38
02	198, 199	3	18	69, 70	21	111	22	der	41	15	29-33	8	36, 37	39-42
03	200-202	4	19	71, 72	22	112	23	Physik.	42	16	33-37	9	37-39	43-46
04	203	5	20	72, 73, 74	23	113	24		43	17	38-42	10	39, 40	47-49
1905	204, 205	6	21	74-76	24	114	25		44	18	43-48	11	40-42	50-53
06	206	7	22	A. 77, 78	25	115	26		45	19	48-52	12	43, 44	54-57
07	207	8	23	78, 79, 80	26	116	27		46	20	52-56	13	45, 46	58-60
08	207-209	9	24	80, 81	27	117	28		47	21	56-60	14	44-46	61-64
09	209, 210	10	25	82, 83	28	118	29		48	22	61-65	15	46, 47	65-69
1910	210	11	26	83, 84	29	119	30		49	23	65-69	16	48, 49	70-74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69-73	17	49, 50	75-77
12	211, 212	13	28	86, 87	31	121	32		51	25	73-79	18	50-52	78-80
13	212, 213	14	29	88, 89	32	122	33		52	26	79-83	19	52, 53	81-86
14	213, 214	15	30	89, 90	33	123	34		53	27	84-90	20	54	86-88
1915	215, 216	16	Publication		34	...	35		54	28	90-93	21	55	89, 90
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19	...	...	abandoned.		38	...	39		58	32	105-109	25	issue*	...

\* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF  
INORGANIC CHEMISTRY.  
VOLUME VII. PART III.



# A TEXT-BOOK OF INORGANIC CHEMISTRY.

## VOL. VII. PART III. CHROMIUM AND ITS CONGENERS.

### CHAPTER I.

#### GENERAL CHARACTERISTICS OF THE ELEMENTS OF GROUP VI., SUBDIVISION A.

THE elements comprising Subdivision A of the sixth group of the Periodic Table form a natural group of four metals, namely, chromium, molybdenum, tungsten, and uranium. The relationships between these

elements and their congeners in Subdivision B are not very marked,<sup>1</sup> but certain close analogies may be observed. It is characteristic of the chromium family that they exhibit various degrees of valency and produce numerous types of stable compounds, but of these the most stable are those containing the elements in the hexavalent condition. The trioxides,  $\text{CrO}_3$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ , and  $\text{UO}_3$ , possess powerful acidic properties and yield well-defined salts, namely, chromates, molybdates, tungstates, and uranates, which are analogous to, and often isomorphous with, the sulphates and selenates. The trioxides, however, are amphoteric, and the basic nature is particularly evident in uranium trioxide, which forms a series of stable *uranyl* salts of the type  $\text{UO}_2\text{X}_2$ , the most important example of which is the nitrate  $\text{UO}_2(\text{NO}_3)_2$ .

Uranium shows an interesting similarity to tellurium in the formation of a sulphate of the type  $\text{M}(\text{SO}_4)_2$ ; it also resembles polonium or radium F, the heaviest member of the oxygen group, in being radioactive.

Chromium shows many similarities to its neighbours in the even series of the first long period:

Group.	IV <sub>A</sub>	V <sub>A</sub>	VI <sub>A</sub>	VII <sub>A</sub>	VIII		
	Ti	V	Cr	Mn	Fe	Co	Ni
Atomic Number.	22	23	24	25	26	27	28.

<sup>1</sup> The general characteristics of the elements of Group VI, taken as a whole are dealt with in Chapter I, of Vol. VII, Part I. Those of Subdivision B are considered in Vol. VII, Part II.

The chromous salts, derived from the oxide  $\text{CrO}$ , are analogous to the salts of divalent vanadium, manganese, and iron. This is seen in the isomorphism of the sulphates of the type  $\text{R} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$ . The stability of such salts increases in the order of the atomic number of the metal. The chief basic oxide of chromium is the sesquioxide  $\text{Cr}_2\text{O}_3$ , which is closely allied to ferric oxide, and, like the latter, resembles aluminium oxide. The hydroxide,  $\text{Cr}(\text{OH})_3$ , with bases yields *chromites* analogous to, but less stable than, the aluminates. Chromic sulphate enters into the formation of alums. The chromic salts are very stable, but in the trivalent condition the metal shows a marked tendency to form complex ions, both anions and cations; thus it resembles iron in producing complex cyanides, whilst it also yields compounds similar to the cobaltamines.

The remaining elements of the group, molybdenum, tungsten, and uranium, exhibit few analogies to their congeners in Subgroup VA, and it is to be observed that the corresponding elements of Subgroup VIIA have not as yet been discovered.<sup>1</sup> The compounds of the elements of the chromium group are generally coloured, and this property appears to be connected with the variable valency displayed by the metals. Vanadium, the compounds of which are highly coloured, affords an interesting analogy in this respect.

Uranium, in the uranous compounds in which the element is tetravalent, appears to be closely allied to thorium, the terminal member of Subgroup IVA. The dioxide,  $\text{UO}_2$ , is isomorphous with thorium oxide,  $\text{ThO}_2$ ; the sulphates are also isomorphous and are only slightly soluble in water. The oxalates of the two elements are highly insoluble. Most uranous salts are readily soluble. Many other salts of tetravalent uranium and thorium are isomorphous; nevertheless the two elements exhibit very considerable differences and can easily be separated.<sup>3</sup>

The elements of the chromium group show themselves much more intimately related to one another, and constitute a true family of elements. They are all true metals, white or grey in colour, not sufficiently hard to scratch glass, and extremely infusible. The more important physical properties are compared in the following table: <sup>4</sup>

	Chromium.	Molybdenum.	Tungsten.	Uranium.
Atomic weight .	52.01	96.0	184.0	238.2
Density . . .	6.9	9-10	19.0	18.7
Specific heat .	0.1208	0.0647	0.0358	0.0280
Melting-point .	1550° C.	2450 ± 80° C.	3267 ± 80° C.	1850° C.
Boiling-point .	2200° C.	3200° C.	4700° C. <sup>5</sup>	<2450° C.

<sup>1</sup> But see Noddack and Taacke, *Chem. News*, 1925, 131, 84; Dolajšek and Heyrovský, *Nature*, 1925, 116, 782; Campbell, *ibid.*, p. 860; Loring, *Chem. News*, 1926, 132, 101; also Ogawa, *J. Coll. Sci. Tokyo*, 1908, 25, xvi., 1; Gerber, *Mon. scient.*, 1917, [5], 7, 73, 121, 169, 219; Barbe, *ibid.*, 1919, [5], 9, i., 73.

<sup>2</sup> Hillebrand, *Zeitsch. anorg. Chem.*, 1893, 3, 243.

<sup>3</sup> See Fleck, *Trans. Chem. Soc.*, 1914, 105, 247.

<sup>4</sup> More complete data are given in the text.

<sup>5</sup> See footnote, p. 187.

The melting-point of tungsten is higher than that of any other known metal. The metals are stable in air at ordinary temperatures, but when heated they exhibit a remarkable difference in behaviour. Uranium burns briskly at  $170^{\circ}\text{C}.$ , producing uranous oxide  $\text{UO}_2$ ; molybdenum at a red heat yields the trioxide  $\text{MoO}_3$ ; chromium only burns at  $2000^{\circ}\text{C}.$  and forms the sesquioxide  $\text{Cr}_2\text{O}_3$ ; tungsten is not oxidised at any temperature, except in the vapour form.

As already indicated, the elements exhibit variable valency and yield trioxides with powerful acidic properties. The lower oxides are predominantly basic. No compounds with hydrogen are known. The elements unite directly with halogens, and numerous halide compounds, which may also be prepared by solution of the metal or an oxide in halogen acid, have been obtained. Many oxyhalides are also known.

The more important types of compounds yielded by the elements are shown in the following table:

Type.	Chromium.	Molybdenum.	Tungsten.	Uranium.
$\text{MF}_6$	..	$\text{MoF}_6$	$\text{WF}_6$	$\text{UF}_6$
$\text{MOF}_4$	..	$\text{MoOF}_4$	$\text{WOF}_4$	..
$\text{MCl}_2$	$\text{CrCl}_2$	$\text{MoCl}_2$	$\text{WCl}_2$	..
$\text{MCl}_3$	$\text{CrCl}_3$	$\text{MoCl}_3$	..	$\text{UCl}_3$
$\text{MCl}_4$	..	$\text{MoCl}_4$	$\text{WCl}_4$	$\text{UCl}_4$
$\text{MO}_2\text{Cl}_2$	$\text{CrO}_2\text{Cl}_2$	$\text{MoO}_2\text{Cl}_2$	$\text{WO}_2\text{Cl}_2$	$\text{UO}_2\text{Cl}_2$
$\text{M}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{Mo}_2\text{O}_3$	..	..
$\text{MO}_2$	$\text{CrO}_2$	$\text{MoO}_2$	$\text{WO}_2$	$\text{UO}_2$
$\text{MO}_3$	$\text{CrO}_3$	$\text{MoO}_3$	$\text{WO}_3$	$\text{UO}_3$
$\text{H}_2\text{MO}_4$	$\text{H}_2\text{CrO}_4$	$\text{H}_2\text{MoO}_4$	$\text{H}_2\text{WO}_4$	$\text{H}_2\text{UO}_4$

Oxides between the dioxides and trioxides are also known. The acids of the type  $\text{H}_2\text{MO}_4$  yield an unusual variety of salts of composition  $\text{R}_2\text{O}_x\text{MO}_3$ ; in the case of molybdenum, salts containing as many as 18 atoms of molybdenum to the molecule have been prepared. This form of condensation is also very marked with tungstic acid, whilst chromic and uranic acids exhibit it in less degree. In addition, molybdic and tungstic acids possess the property of combining with certain acidic oxides in varying proportions, with formation of complex acids from which series of well-defined salts may be obtained. Such oxides as phosphoric, arsenic, and boric oxides readily take part in such combinations. Molybdo-phosphoric acids containing the two oxides in the following proportions:  $\text{P}_2\text{O}_5 : \text{MoO}_3 :: 1 : 24, 1 : 18, \text{ and } 1 : 17$ , are known; whilst derivatives of molybdo-arsenic acids, containing the oxides,  $\text{As}_2\text{O}_5$  and  $\text{MoO}_3$ , in the proportions  $1 : 24, 1 : 20, 1 : 18, 1 : 16, \text{ and } 1 : 6$ , have been described. Corresponding tungsto-compounds also exist. An interesting type of isomorphism is met with in some of these complex derivatives, the isomorphous compounds containing different numbers of atoms in the molecules. Thus the two potassium salts,  $4\text{K}_2\text{O} \cdot 0.2\text{SiO}_2 \cdot 24\text{WO}_3 \cdot 36\text{H}_2\text{O}$  and  $5\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot 36\text{H}_2\text{O}$ , are isomorphous.<sup>1</sup>

<sup>1</sup> On the constitution of these compounds, and for other examples of such isomorphism, see pp. 234-5, 205.

Various sulphides of the chromium elements exist, and these, particularly in the case of molybdenum and tungsten, combine with alkalies and alkali sulphides to produce thio-salts; thus, thio-tungstates of the types  $R'_2WO_3S$ ,  $R'_2WO_2S_2$ ,  $R'_2WOS_3$ , and  $R'_2WS_4$ , have been prepared.

By the action of hydrogen peroxide on the trioxides or their derivatives, highly oxidised compounds are obtained. These appear to be of several different types, and their constitution, which has not as yet been completely elucidated, is discussed in other chapters. It is possible that in such compounds the valency of the metal may exceed 6; there is ground for this belief, especially in the case of the perchromates. There is as yet, however, need for further evidence before it can be definitely stated that any of the members of this group exhibit a valency greater than 6.

## CHAPTER II.

### CHROMIUM.

Symbol, Cr. Atomic weight, 52.01.

**Occurrence.**—Chromium does not occur in the free state in nature. The chief mineral from which the metal is obtained is variously known as *chromite*, *chrome iron ore*, *chromoferrite*, or *siderochrome*,  $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ ,<sup>1</sup> and is widely distributed, particularly in serpentine and olivine rocks. It is found in Algeria, Asia Minor, Canada, France, Greece, India, New Caledonia, Rhodesia, the Shetland Islands, Sweden,<sup>2</sup> the Transvaal, Turkey, and the United States.<sup>3</sup> Rhodesia is the chief producer in normal times, but in the later years of the European war the United States and India produced enormous quantities.<sup>4</sup> A deposit of chrome iron ore, containing about 85 per cent. of  $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ , has been found in the province of Kuban, Northern Caucasus.<sup>5</sup> Platiniferous chromites occur in the Ural Mountains.<sup>6</sup> Small quantities of chromite are present in many meteorites.<sup>7</sup> Chromite occurs in octahedra, but is generally found in a brownish-black massive form, having a granular or compact structure. It is sometimes feebly magnetic, of density 4.82 to 4.57, and is one of the heaviest as well as one of the softest minerals of the spinel group, its hardness being about 5.5 according to Mohs' scale.<sup>8</sup> A specimen from the Urals was found to melt at  $1850^\circ \text{C}$ .,<sup>9</sup> but the usual melting-point range is from  $1545^\circ \text{C}$ . to  $1730^\circ \text{C}$ .<sup>10</sup> *Magnochromite* and *chromopicrotite* are varieties of chromite. The latter occurs at Dun Mountain, New Zealand, and in the Lillooet District, British Columbia, where it is found in velvet-black, massive, coarsely granular veins, and has a density of 4.239.<sup>11</sup> A chromiferous iron ore, containing up to 50 per cent. of iron and varying amounts of chromium up to about 3 per cent., is mined to a considerable extent in Greece<sup>12</sup> and is also employed as a source of chromium.

<sup>1</sup> For an account of spectroscopic analyses of various samples of chromite, see Rubies, *Anal. Fis. Quim.*, 1917, 15, 61.

<sup>2</sup> Tönggron, *Teknisk Tidskrift*, 1913, 43, 26.

<sup>3</sup> See report by Phalen, *U.S. Geol. Survey*, 1912; *Mineral Resources for 1911*, part 1, p. 979.

<sup>4</sup> See Rumbold, *Chromium Ore*, Monograph on Mineral Resources, Imperial Inst., 1921; also Williams, *Chem. News*, 1918, 117, 348.

<sup>5</sup> Besborodko, *Jahrb. Miner.*, 1912, 34, 783.

<sup>6</sup> Vogel, *Jahresber.*, 1873, p. 291; Duparc and Rubies, *Anal. Fis. Quim.*, 1913, 11, 367.

<sup>7</sup> Tassin, *Proc. U.S. National Museum*, 1908, 34, 685; Borgström, *Zeitsch. Kryst. Min.*, 1910, 48, 540, from *Geol. För Stockholm Förhandl.*, 1908, 30, 331.

<sup>8</sup> For Mohs' scale, see this series, Vol. IX., Part II., p. 11, footnote.

<sup>9</sup> Brun, *Arch. Sci. phys. nat.*, 1902, [4], 13, 352.

<sup>10</sup> Patterson, *J. Iron Steel Inst.*, Carnegie Memoirs, 1914, 6, 238.

<sup>11</sup> Hoffmann, *Amer. J. Sci.*, 1902, [4], 13, 242.

<sup>12</sup> See *Bulletin of the Imperial Institute*, 1910, 8, 278.



*Crocoite*, *crocoisite*, *chrombleispath*, or *rothbleierz* is a natural form of lead chromate,  $\text{PbCrO}_4$ . It was discovered at Berezov in Siberia, but is also found in Brazil, Swaziland, Tasmania, and, associated with galena, in the Lydenburg district of the Transvaal. It occurs in translucent, hyacinth-red crystals of adamantine lustre; density 6.00. Crocoite crystallises in the monoclinic system, usually prismatic, its crystallographic elements being

$$a : b : c = 0.960842 : 1 : 0.915856; \beta = 77^\circ 32' 50''.$$

*Phenicochroite* or *melanochroite*, of density 5.75, is a basic chromate of lead,  $3\text{PbO} \cdot 2\text{CrO}_3$ , and is probably orthorhombic. *Beresovite* or *beresovite* contains lead carbonate as well as the chromate.<sup>1</sup> *Vauquelinite*, probably identical with *laumannite*, is a phospho-chromate of lead and copper,  $2(\text{Pb}, \text{Cu})\text{CrO}_4 \cdot (\text{Pb}, \text{Cu})_3(\text{PO}_4)_2$ ,<sup>2</sup> of a greenish or brownish colour, occurring in the quartz of Berezov (Urals). It forms monoclinic crystals of density 5.95:

$$a : b : c = 0.74977 : 1 : 1.39083; \beta = 69^\circ 3'.$$

*Chromitite* is obtained as a small-grained black sand, of density 3.1, from Kopaonik Mountain, Serbia, and has the composition  $(\text{Fe}, \text{Al})_2\text{O}_3 \cdot 2\text{Cr}_2\text{O}_3$ .<sup>3</sup> It resembles magnetite, being magnetic and crystallising in the cubic system.

*Chromium mica* or *fuchsinite*<sup>4</sup> possesses a brilliant green colour; *chrome ochre* is a bright green, clayey mineral containing  $\text{Cr}_2\text{O}_3$ . *Alexandrolite*, *milosin*, *wolchonskoite*, and *avalite* contain hydrated oxides of chromium, aluminium, and silicon.<sup>5</sup> *Dietzeite* contains calcium iodate and chromate.

Chromium also occurs in the following minerals: *daubreelite*,  $\text{FeS} \cdot \text{Cr}_2\text{S}_3$ , massive, brittle, non-magnetic, density 5.01; *redingtonite*, a hydrated chromium sulphate; *tarapacite*, essentially a chromate of potassium; and *chrome-diopside*, a pyroxene from Kimberley.

A nickel-chrome spinel,  $\text{NiO} \cdot \text{Cr}_2\text{O}_3$ , has been made artificially in small green crystals.<sup>6</sup> The green colour of emerald, serpentine, possibly sapphire,<sup>7</sup> and other minerals is due to the presence of compounds of chromium, which also occur in rubies, corundums, and spinels. It has been shown<sup>8</sup> that the peculiar spectra of ruby and diamond are due to chromium oxide which has been compelled to vibrate in an abnormal manner, leading to the production of narrow absorption bands. Traces of chromium have been detected in the soot produced by the combustion of coal obtained from deposits at Liège.<sup>9</sup> Compounds of chromium are not known to play any part in the economy of plants or animals.

**Early History.**—Lehmann, writing in 1762 to de Buffon, described a new mineral from Siberia, now known as crocoite (*q.v.*). On examination of this mineral by Vauquelin and Macquart in 1789, lead, iron,

<sup>1</sup> Samoilow, *Bull. Soc. Moscow*, 1897, p. 290.

<sup>2</sup> Rammeisberg, *Handbuch der Mineralchemie*, 1875, ii., 281; Suppl., 1886, 198; 1895, 115.

<sup>3</sup> Jovitschitsch, *Monatsh.*, 1900, 30, 39; *Bull. Soc. franç. Min.*, 1912, 35, 511.

<sup>4</sup> Sandberger, *Jahrb. Miner.*, 1879, p. 307.

<sup>5</sup> Losanitsch, *Chem. News*, 1894, 69, 243; *Ber.*, 1895, 28, 2631.

<sup>6</sup> Guertler, *German Patent*, 182200 (1907).

<sup>7</sup> Moir, *Trans. Roy. Soc. S. Africa*, 1918, 7, 129.

<sup>8</sup> Dubois, *Ber.*, 1898, 31, 1977.

<sup>9</sup> Jorissen, *Bull. Acad. roy. Belg.*, 1905, p. 178.

and alumina were reported; chromium was not detected till 1797 when, on reinvestigation, Vauquelin<sup>1</sup> observed that the lead was combined with a new acid derived from the oxide of a hitherto unknown metallic element. On account of the fact that its compounds are all coloured, the name chromium (Greek *chroma*, colour) was given to the element in question. In 1798, Vauquelin detected the new element in spinel and in smaragdite, and the following year Tassaert found it in chrome iron ore. The discovery of chromium in crocoite was made simultaneously and independently by Klaproth.<sup>2</sup> More recent work has dealt largely with the isomerism exhibited by chromium compounds, and the relation between their colour and constitution.

**Preparation.**—Metallic chromium is usually obtained by reduction of the sesquioxide,  $\text{Cr}_2\text{O}_3$ , the chief source of which is chrome iron ore (p. 7). The latter, after separation from gangue, is powdered, washed, mixed with lime and potassium carbonate, dried, and then roasted, the mass being continually stirred. The potassium chromate produced is extracted with water and converted into the dichromate by treatment with sulphuric acid. After recrystallisation the potassium dichromate is reduced by heating with sulphur, starch, or other suitable material, and finally washed with water; the chromium sesquioxide remains undissolved.

1. *Reduction of Chromium Sesquioxide with Carbon.*—Deville,<sup>3</sup> by strongly heating the oxide with sugar charcoal in a brasqued lime crucible, obtained small quantities of metallic chromium contaminated with carbide and silicide. The reaction is never quite quantitative.<sup>4</sup> The reduction was effected by Moissan<sup>5</sup> in an electric arc furnace, when a product containing a considerable proportion of carbon was obtained. This was eliminated by re-fusing with lime, calcium carbide being formed, and then again fusing the product in a crucible brasqued with the double oxide of calcium and chromium.

2. *Reduction of Chromium Sesquioxide by Metals.*—The reduction can be effected by the alkali metals, magnesium, and aluminium.<sup>6</sup> Goldschmidt's aluminothermic process consists in mixing the requisite proportions of chromium sesquioxide and aluminium powder, placing the mixture—covered first with a layer of mixed barium peroxide and aluminium powder, and finally with a layer of powdered fluorspar—in a magnesia or refractory clay crucible, and igniting with a "fuse" of magnesium ribbon. The temperature developed by the combustion of

<sup>1</sup> Vauquelin, *Ann. Chim. Phys.*, 1798, 25, 21, 104; 1800, 70, 70; *Crell's Annalen*, 1798, 1, 183, 276.

<sup>2</sup> Roscoe and Schorlemmer, *Treatise on Chemistry* (Macmillan), 1907, ii., 995. Investigations were also conducted by Unverdorben, *Trommsd. N.J. Pharm.*, 1826, 9, 1, 26; Mussin-Puschin, *Crell's Annalen*, 1798, 1, 365; 2, 444. The composition, constitution, and properties of its salts have been studied by Berzelius, *Schweigger's J.*, 1818, 22, 53; *Ann. Chim. Phys.*, 1821, 17, 7; *Pogg. Annalen*, 1824, 1, 34; *Annalen*, 1844, 49, 247; Branderburger, *Schweigger's J.*, 1815, 13, 274; Döbereiner, *ibid.*, 1818, 22, 470; Meissner, *Gilbert's Annalen*, 1818, 60, 366; Laimaquo, *Ann. Chim. Phys.*, 1820, 14, 209; Berthier, *ibid.*, 1821, 17, 56; Grouvelle, *ibid.*, 1821, 17, 349; Thomson, *Ann. Phil.*, 1820, 16, 321; Unverdorben, *loc. cit.*; Moser, *Abhandl. über das Chrom*, Vienna, 1824; Maus, *Pogg. Annalen*, 1827, 9, 127; 11, 83; Rose, *ibid.*, 1833, 27, 505; 1838, 45, 183.

<sup>3</sup> Deville, *Ann. Chim. Phys.*, 1866, [3], 46, 182; *Compt. rend.*, 1867, 44, 673.

<sup>4</sup> Greenwood, *Trans. Chem. Soc.*, 1908, 93, 1488.

<sup>5</sup> Moissan, *Compt. rend.*, 1893, 116, 394; 1894, 119, 185; *Ann. Chim. Phys.*, 1896, [7], 8, 559.

<sup>6</sup> Moissan, *Compt. rend.*, 1896, 122, 1302; Goldschmidt, *J. Soc. Chem. Ind.*, 1898, 17, 543.

the barium peroxide-aluminium mixture is sufficiently high to cause a violent, often explosive, reduction of the chromium sesquioxide; it is consequently necessary for the operator to protect his face and hands. The alumina remains on the surface as a slag, which crystallises on cooling, forming *corubin*, while the chromium is found at the bottom of the crucible as a metallic button.

On the manufacturing scale, about 100 kilos. of chromium are produced in a single operation. It is preferable to use a mixture of chromium sesquioxide and trioxide (or potassium dichromate) instead of the sesquioxide alone for incorporation with aluminium powder.<sup>1</sup> Suitable proportions are: 20 grams of a mixture containing 50 grams of fused powdered potassium dichromate with 18 grams of aluminium powder, together with 100 grams of a mixture containing 160 grams of dry aluminium powder with 450 grams of calcined chromium sesquioxide.<sup>2</sup> Commercially, pure carbon-free chromium is produced only by reduction of chromium oxide with aluminium.<sup>3</sup>

Chromium can also be obtained by reduction of the chloride or of chromates, from the boride, and by electrolytic methods.

8. *Reduction of Chromic Chloride, CrCl<sub>3</sub>.*—Wöhler<sup>4</sup> obtained metallic chromium by reduction of chromic chloride with potassium, while Frémy<sup>5</sup> obtained the metal in a crystalline condition by passing sodium vapour over chromic chloride in an atmosphere of pure dry hydrogen. Wöhler<sup>4</sup> prepared similar crystals—minute octahedra—by fusion of chromic chloride with zinc under a layer of mixed sodium and potassium chlorides, and removal of the zinc from the alloy so formed by means of nitric acid.<sup>7</sup> Metallic calcium reduces chromic chloride at a dull red heat without formation of an alloy.<sup>8</sup>

4. *Electrolytic Methods.*<sup>9</sup>—Electro-deposition of metallic chromium from a solution of chromic chloride was accomplished by Bunsen,<sup>10</sup> who obtained a coherent deposit of the metal possessing a bright surface and in appearance somewhat resembling iron.<sup>11</sup> It has been observed<sup>12</sup> that in the electrolytic deposition of chromium from solutions of chromic salts, green solutions are first converted into violet solutions, the chromium being deposited from the latter and not from the former modification. Chromium is deposited from solutions of chromic acid by electrolysis, especially in presence of sulphuric acid. Chromic salts are simultaneously formed, and the solution becomes brown during the electrolysis, which proceeds more readily with impure chromic acid than with pure.<sup>13</sup> The best results appear to be obtained by using a

<sup>1</sup> Vigouroux, *Bull. Soc. chim.*, 1907, [4], 1, 10; Olie, *Chem. Weekblad*, 1906, 3, 662.

<sup>2</sup> Olie, *loc. cit.*

<sup>3</sup> Richards, *Metallurgical and Chemical Engineering*, 1916, 15, [1], 26.

<sup>4</sup> Wöhler, *Annalen*, 1859, 111, 117, 230.

<sup>5</sup> Frémy, *Compt. rend.*, 1857, 44, 633.

<sup>6</sup> Wöhler, *loc. cit.*

<sup>7</sup> See also Zettnow, *Pogg. Annalen*, 1871, 143, 477; Jäger and Krüss, *Ber.*, 1889, 22, 2052; Glatzel, *ibid.*, 1890, 23, 3127; Prinz, *Compt. rend.*, 1893, 116, 392.

<sup>8</sup> Hackspill, *Bull. Soc. chim.*, 1907, [4], 1, 895.

<sup>9</sup> See Askenazy and Révai, *Zeitsch. Elektrochem.*, 1913, 19, 344.

<sup>10</sup> Bunsen, *Pogg. Annalen*, 1854, 91, 619.

<sup>11</sup> See also Férée, *Bull. Soc. chim.*, 1901, [3], 25, 617. Placet (*Compt. rend.*, 1892, 115, 945) similarly decomposed chrome alum.

<sup>12</sup> Dony-Henault, *Zeitsch. Elektrochem.*, 1906, 12, 329.

<sup>13</sup> Carvoth and Curry, *J. Physical Chem.*, 1905, 9, 353; Carvoth and Mott, *ibid.*, 1905, 9, 232.

solution containing chromic acid (245 grams per litre) and chromium sulphate (8 grams per litre), with a current density of 13.4 amperes per square decimetre.<sup>1</sup> Such solutions, with chromium anodes, may be used for plating iron and steel. The anodes show no tendency to become passive, and the coatings obtained are stated to be very resistant to acids and to atmospheric corrosion. Electrolysis of the fused salts is difficult because of their high melting-points.

5. *Other Methods*.—Crystalline chromium has been obtained<sup>2</sup> by reduction of lead chromate in a brasqued crucible. A concentrated solution of chromic chloride, when treated with sodium amalgam, yields a chromium amalgam which, on distilling at 350° C. in hydrogen, or at lower temperatures in a vacuum, leaves a residue of amorphous chromium which under some conditions is pyrophoric.<sup>3</sup> Fusion of chromium boride with metallic copper gives metallic chromium.<sup>4</sup> Reduction of the sesquioxide at 1500° C. with pure hydrogen yields the metal in a very pure condition.<sup>5</sup> Various modifications of and alternatives for the above methods have been suggested.<sup>6</sup>

**Physical Properties**.—Chromium was not for some considerable period obtained in a pure state, being always contaminated with carbon, silicon, aluminium, iron, etc., incidental to the method of preparation. That obtained by Vigouroux<sup>7</sup> contained 0.36 to 0.4 per cent. silicon and 0.74 to 0.85 per cent. aluminium and iron, though it was free from carbon. Moreover, some processes furnished the impure metal in an amorphous or porous condition, while in others the crystalline form was produced. Thus it is evident that a certain discord among the observed data is to be anticipated.<sup>8</sup> The appearance and form of pure chromium have been variously described; for example, as grey rhombohedra;<sup>9</sup> as tetragonal pyramids;<sup>10</sup> as a microscopically crystalline grey powder;<sup>11</sup> as tin-white rhombohedra;<sup>12</sup> as fusible crystals.<sup>13</sup> A recent X-ray examination of the crystal structure of a specimen of chromium has revealed the presence of two allotropes of the metal.<sup>14</sup> Moissan<sup>15</sup> has prepared a pyrophoric form by distilling the amalgam at 300° C. *in vacuo*.

The hardness of metallic chromium measured on Rydberg's system is 9.0,<sup>16</sup> though pure chromium prepared by Moissan did not scratch

<sup>1</sup> Schwartz, *J. Amer. Electrochem. Soc.*, 1923, 44, 461; Sargent, *ibid.*, 1920, 37, 470. See also Liebreich, *Zeitsch. Elektrochem.*, 1921, 27, 94.

<sup>2</sup> Debray, see Wurtz, *Dictionnaire de Chimie*, 1867, 1, 885.

<sup>3</sup> Moissan, *Compt. rend.*, 1896, 122, 1302; Féreé, *ibid.*, 1895, 121, 822; Vincent, *Jahresber.*, 1892, p. 146; Roussin, *ibid.*, 1896, p. 170.

<sup>4</sup> du Jassonneix, *Compt. rend.*, 1907, 144, 915.

<sup>5</sup> Rohn, *Zeitsch. Metallkunde*, 1924, 16, 275.

<sup>6</sup> Rouff, *Ber.*, 1888, 21, 383; Féreé, *Bull. Soc. chim.*, 1901, [3], 25, 617; Mohorg, *J. prakt. Chem.*, 1848, 44, 322; Weiss and Aichel, *Annalen*, 1904, 337, 370.

<sup>7</sup> Vigouroux, *Bull. Soc. chim.*, 1907, [4], 1, 10.

<sup>8</sup> See Berzelius, *Annalen*, 1844, 49, 247; Ostwald, *Zeitsch. physikal. Chem.*, 1900, 35, 33, 204; Brauer, *ibid.*, 1901, 38, 441; Döring, *J. prakt. Chem.*, 1902, 66, 65; Carveth and Mott, *J. Physical Chem.*, 1905, 9, 231.

<sup>9</sup> Wöhler, *Annalen*, 1859, 111, 117, 230.

<sup>10</sup> Bolley, *Quart. J. Chem. Soc.*, 1860, 13, 333.

<sup>11</sup> Glatzel, *Ber.*, 1890, 23, 3127.

<sup>12</sup> Jäger and Krüss, *ibid.*, 1889, 22, 2052.

<sup>13</sup> Moissan, *Bull. Soc. chim.*, 1879, [2], 31, 149; *Compt. rend.*, 1893, 116, 349; 1891, 119, 185; *Le four électrique*, 1897.

<sup>14</sup> Bradley and Ollard, *Nature*, 1926, 117, 122.

<sup>15</sup> Moissan, *Ann. Chim. Phys.*, 1880, [5], 21, 199; Féreé, *Compt. rend.*, 1895, 121, 822.

<sup>16</sup> See Rydberg, *Zeitsch. physikal. Chem.*, 1900, 33, 363. The system, which is based on Mohs' scale, gives a numerical value for the hardness of the elements.

glass. The density of chromium<sup>1</sup> at 16° C. is 6.72, while for the pure metal (previously fused in the electric oven) at 20° C. the value 6.92 was obtained.<sup>2</sup> Jassonneix<sup>3</sup> obtained the value 7.1 at 17° C. for a specimen obtained from the boride. The mean specific heat of metallic chromium between 0° C. and 98.24° C. is 0.1216;<sup>4</sup> between 0° C. and 100° C., 0.1208.<sup>5</sup> The specific heats at temperatures ranging from 0° C. to 500° C. of chromium, containing 1.8 per cent. Fe and 0.09 per cent. Si, have been determined<sup>6</sup> as follows:

Temperature, ° C.	Specific Heat.
0	0.1089
100	0.1121
200	0.1176
300	0.1236
400	0.1334
500	0.1503

Electrolytically deposited chromium occludes 250 times its own volume of hydrogen.<sup>7</sup> At ordinary temperatures chromium does not exhibit magnetic properties,<sup>8</sup> but does so at -15° C. to -20° C. The electrical conductivity of powdered chromium is approximately 38.5 mhos per cm. cube.<sup>9</sup>

The melting-point of the metal has been variously recorded as 1489° C.,<sup>10</sup> 1513° C.,<sup>11</sup> 1553° C.,<sup>12</sup> 1547° C.,<sup>13</sup> and 1550° C.<sup>14</sup> Like certain other properties of chromium, the melting-point is profoundly affected by the presence of impurities. Thus a sample of chromium made by the aluminothermic process and containing 1 per cent. of impurity was found<sup>15</sup> to melt at 1515±5° C. The boiling-point of chromium is 2200° C.<sup>16</sup> It can be distilled in the electric furnace, when a crystalline variety is obtained having the same chemical properties as the finely powdered metal.<sup>17</sup>

<sup>1</sup> Glatzel, *loc. cit.*

<sup>2</sup> Moissan, *Compt. rend.*, 1893, 116, 349. See also Wöhler, *Annalen*, 1859, 111, 117, 230; Bunsen, *Pogg. Annalen*, 1854, 91, 619.

<sup>3</sup> du Jassonneix, *Compt. rend.*, 1907, 144, 915.

<sup>4</sup> Jäger and Krüss, *Ber.*, 1889, 22, 2052.

<sup>5</sup> Moche, *Sitzungsber. K. Akad. Wiss. Wien*, 1897, 106, 11A, 590. For specific heats at lower temperatures see Richards and Jackson (*Zeitsch. physikal. Chem.*, 1910, 70, 414), Schimpf (*ibid.*, 1910, 71, 257), Nordmeyer and Bernoulli (*Ber. Deut. physikal. Ges.*, 1907, 9, 175), Forel and Nordmeyer (*Ann. Physik*, 1906, [4], 20, 423).

<sup>6</sup> Adler, *Ann. Physik, Beibl.*, 1903, 27, 330.

<sup>7</sup> Carveth and Curry, *J. Physical Chem.*, 1905, 9, 353.

<sup>8</sup> Moissan, *loc. cit.*; Glatzel, *loc. cit.*; Wöhler, *loc. cit.*; see also Faraday, *Phil. Trans.*, 1840, 136, 41; Wiedemann, *Pogg. Annalen*, 1834, [2], 32, 452; Weiss and Omnes, *Compt. rend.*, 1910, 150, 687.

<sup>9</sup> Shukoff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 40.

<sup>10</sup> Burgess, *Bureau Stand.*, Washington, 1907, 3, [3], 345.

<sup>11</sup> Troitschke and Tammann, *Zeitsch. anorg. Chem.*, 1907, 55, 402.

<sup>12</sup> Williams, *ibid.*, 1907, 55, 1; Voss, *ibid.*, 1908, 57, 58.

<sup>13</sup> Lewkonja, *ibid.*, 1908, 59, 293.

<sup>14</sup> Lewis, *Chem. News*, 1902, 86, 13.

<sup>15</sup> Greenwood, *Proc. Roy. Soc.*, 1909, A, 82, 390; 1910, A, 83, 483.

<sup>17</sup> Moissan, *Compt. rend.*, 1908, 142, 425.

*Spectrum*.—Compounds of chromium impart no distinctive colour to the non-luminous flame. The spectrum, however, is somewhat complicated, especially the spark spectrum. Careful and complete measurements have been made, for which the reader is referred to the literature.<sup>1</sup>

Exner and Haschek (*loc. cit.*) state that the most intense lines ("hauptlinien") in the arc and spark spectra are as follows: <sup>2</sup>

Arc Spectrum.		Spark Spectrum.	
Wave-Length.	Intensity (Max. = 100).	Wave-Length.	Intensity (Max. = 100).
3578.81	30 <i>u</i> *	2677.27	20 *
3598.64	30 <i>u</i> *	2880.63	20
3506.49	30 <i>u</i> *	2885.71	30
4254.51	50 <i>u</i> *	3125.11	20 *
4275.00	50 <i>u</i>	3132.20	20 *
4289.90	50 <i>u</i> *	3360.50	20 †
[4646.31]	2	3368.19	20 *
4646.35	20	3408.90	20 † *
5204.71	20 *	3422.89	20 †
5206.24	30 <i>u</i> *	3578.81	20 <i>u</i>
5208.00	30 <i>u</i> *	[3578.86]	3
[5345.95]	1	3598.63	20 <i>u</i>
5345.99	20	[3598.67]	3
5410.01	20 *	[3605.44]	1
		3605.48	20
		4254.50	50 *
		4274.95	30 *
		4289.89	30
		4558.80	20
		4588.43	20
		5208.61	20 *

It does not follow, however, that those lines which are greatest in *intensity* are the most *persistent*. The spark spectrum of chromium has been studied quantitatively by Pollok and Leonard<sup>3</sup> from this point of view, and the residuary lines (those last to disappear upon dilution) recorded. Their method of procedure was as follows:

There was made a concentrated or saturated solution of chromic chloride, as well as solutions containing 1 gram of the element in 100,

<sup>1</sup> See Huggins, *Pogg. Annalen*, 1865, 124, 275, 321; Thalen, *Ann. Chim. Phys.*, 1869, [4], 18, 202; Lecoq de Boisbaudran, *Les spectres lumineux*; Adeney, *Sci. Proc. Roy. Dubl. Soc.*, 1904, 10, 235; Miller, *Ann. Physik*, 1907, [4], 24, 105; Roscoe and others, *Brit. Assoc. Rep.*, 1900, 76, 161; Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1907, [2], 11, 217; Purvis, *Proc. Camb. Phil. Soc.*, 1907, 14, 41; Stütting, *Zeitsch. wiss. Photograph., Photo-physik, Photochem.*, 1909, 7, 73; Siegbahn and Stenström, *Physikal. Zeitsch.*, 1916, 17, 48; Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Vienna, 1911); and other standard works on Spectroscopy. The infra-red spectrum of chromium has been studied by Randall and Barker, *Astrophys. J.*, 1919, 49, 54.

<sup>2</sup> The following abbreviations, etc., are employed:—*u*=reversed; †=diffuse; \* =not displaced; [ ] =  $\lambda$  of displaced line at low intensity.

<sup>3</sup> Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1907, 11, 217.

1000, 10,000, and 100,000 parts of solution. Gold electrodes were used,<sup>1</sup> and a photograph of the spark between them was first taken using a long slit; the slit was then shortened and the chromium solution sparked, thus giving the spectrum of gold with long lines and the spectrum of chromium with short lines. The process was then reversed, the chromium being taken long and the gold short, so that any lines coincident with the gold lines might be seen. A photograph was next taken with both the concentrated solution and the gold electrodes long and the metal itself short, to show any lines developed by the chromium, but not by its solutions. Then the last four spectra taken gave the gold electrodes long, with short lines between, of the spark spectra of solutions containing 1, 0.1, 0.01, and 0.001 per cent. of the chromium respectively.

The results obtained were as follows : <sup>2</sup>

### QUANTITATIVE SPECTRUM OF $\text{CrCl}_3$ .

Wave-Length.	Intensity and Persistency.	Wave-Length.	Intensity and Persistency.
4289.9	10 $\psi$	8080.4	} Group $\phi$ .
4274.9	10 $\psi$	8015.8	
4254.5	10 $\psi$	2988.8	
3605.5	10 $\chi$	2980.9	
3598.6	10 $\chi$	2971.9	
3578.8	10 $\chi$	2958.4	
3480.5	10 $\phi$	2843.8	
3422.9	10 $\phi$	2835.2	
3421.4	10 $\phi$	2830.5	
3408.9	10 $\phi$	2766.6	
3408.5	10 $\phi$	2762.7	
3180.8	10 $\phi$	2698.8	
3182.2	10 $\phi$	2663.6	
3050.9	8 $\phi$	2659.0	
		2653.6	

It has been found<sup>3</sup> that the majority of the enhanced lines of chromium occur in the solar Fraunhofer spectrum, although some appear to be missing.

*Absorption Spectrum.*—It has been stated<sup>4</sup> that all solutions of violet salts of chromium show similar absorption due to the chromium

<sup>1</sup> See Hartley, *Phil. Trans.*, 1884, 85, 49.

<sup>2</sup> The following marks of identification are employed :—

$\tau$  = seen with the metal, but not with concentrated solutions.

$\sigma$  = " " concentrated solutions, but not with 1.0 per cent. solutions.

$\phi$  = " " 1.0 per cent. " " " 0.1 " "

$\chi$  = " " 0.1 " " " " 0.01 " "

$\psi$  = " " 0.01 " " " " 0.001 " "

$\omega$  = " " 0.001 " " " " " "

<sup>3</sup> Lockyer and Baxandall, *Proc. Roy. Soc.*, 1904, 74, 255.

<sup>4</sup> Byk and Jaffe, *Zeitsch. physikal. Chem.*, 1909, 68, 323.

ion. The band extends from  $461\mu$  to  $364.5\mu$ , while the beginning of complete absorption is at  $260\mu$  in half-molar solution. In solutions of green complex salts of chromium, the absorption band and the limit of complete absorption are both inclined towards the red.<sup>1</sup>

The absorption of X-rays by chromium in the form of potassium chromate has been studied.<sup>2</sup>

**Chemical Properties.**<sup>3</sup>—Chromium is oxidised only to a very slight extent by moist air at ordinary temperatures, but when heated to  $2000^{\circ}$  C. in oxygen it burns with scintillations of extreme brilliance, forming the sesquioxide,  $\text{Cr}_2\text{O}_3$ . In sulphur vapour at  $700^{\circ}$  C. and in hydrogen sulphide at  $1200^{\circ}$  C., the sulphide is formed; at the latter temperature the metal is attacked superficially by carbon dioxide, whilst on heating with carbon, crystalline carbides are obtained. With silicon and boron, the silicide and boride are respectively formed; anhydrous hydrogen chloride reacts at a red heat with the formation of crystalline chromous chloride,  $\text{CrCl}_2$ , chlorine similarly yielding chromic chloride,  $\text{CrCl}_3$ .

By hydrochloric acid the metal is attacked slowly in the cold, though more quickly on warming.<sup>4</sup> Boiling concentrated sulphuric acid yields sulphur dioxide with the formation of a dark coloured solution; somewhat diluted acid yields hydrogen and chromous sulphate; fuming nitric acid has no action on chromium, neither has aqua regia. The metal is obtained in a *passive* state by exposure to air, concentrated nitric acid, or to other oxidising agents. The passivity has been ascribed to the formation of a superficial layer of an oxide, or possibly of gas, since, when rendered passive by means of nitric acid, the metal contains occluded oxygen and nitric oxide.<sup>5</sup>

Powdered chromium is slowly attacked by mercuric chloride in solution, with the formation of chromic chloride. Though unattacked by fused sodium carbonate, fused potassium nitrate and chlorate oxidise it vigorously. Pyrophoric chromium (see p. 11) combines with nitrogen on heating.<sup>6</sup>

**Uses.**—Metallic chromium is used industrially in the manufacture of certain varieties of steel.<sup>7</sup> It enters into the composition also of many non-ferrous alloys (see p. 17), the importance of which is increasing. It may be used as a protective coating for metals, either in the form of chromium plate (see p. 10), or by causing the metal to diffuse into other metals at temperatures below their melting-points;

<sup>1</sup> For earlier work on the absorption spectra of chromium salts, see Vierordt, *Ber.*, 1872, 5, 34; Alrojd, *Phil. Mag.*, 1876, [5], 2, 423; Bayley, *J. Chem. Soc.*, 1880, 37, 828; Zimmermann, *Annalen*, 1882, 213, 285; Carnelley, *Ber.*, 1884, 17, 2152; Nichols, *Jahresber.*, 1884, p. 296; Sabatier, *Compt. rend.*, 1886, 103, 49, 138; Vogel, *Prakt. Spektralanalyse*, p. 253; Flame spectrum, Vogel, *Ber.*, 1888, 21, 2030; Fluorescence spectrum, Lecoq de Boisbaudran, *Compt. rend.*, 1886, 103, 1107; 1887, 104, 330; 1888, 105, 261.

<sup>2</sup> Fricke, *Phys. Review*, 1920, [2], 16, 202.

<sup>3</sup> See Moissan, *Bull. Soc. chim.*, 1870, [2], 31, 140; *Compt. rend.*, 1893, 116, 349; 1894, 119, 185.

<sup>4</sup> Döring, *J. prakt. Chem.*, 1902, [2], 66, 65.

<sup>5</sup> Hittorf, *Zeitsch. physikal. Chem.*, 1898, 25, 729; 1899, 30, 481; Ostwald, *ibid.*, 1900, 35, 33, 204; Morgan and Duff, *J. Amer. Chem. Soc.*, 1900, 22, 331; Branner, *Zeitsch. physikal. Chem.*, 1901, 38, 441; Döring, *loc. cit.*; Bernoulli, *Physikal. Zeitsch.*, 1904, 5, 632; Fredenhagen, *Zeitsch. physikal. Chem.*, 1908, 63, 1; Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 812, 1119; 21, 138. See also this series, Volume IX., Part II., pp. 55-60, where the passivity of iron is discussed.

<sup>6</sup> Bérce, *Compt. rend.*, 1895, 121, 822.

<sup>7</sup> See this series, Volume IX., Part III.



the latter process is known as *chromising*.<sup>1</sup> Compounds of chromium enter largely into the manufacture of aniline black and of certain insoluble pigments, into photography, dyeing, and tanning<sup>2</sup> (see p. 68).

Chromite is used in steel works as a refractory material for lining and repairing basic hearth furnaces. In its resistance to corrosion, and durability, it is superior to magnesite and silica-alumina mixtures. It withstands sudden temperature changes, resists abrasion, and its hardness is but little affected at high temperatures.

The stimulative and toxic effects of compounds of chromium have been investigated.<sup>3</sup>

**Atomic Weight.**—From a consideration of the vapour densities of volatile compounds of chromium, and from the application of Dulong and Petit's Law, it is obvious that the atomic weight of chromium is about 52—that is, three times the chemical equivalent of chromium in chromic salts, or six times its combining weight in derivatives of chromium trioxide. Chromium thus exhibits di-, tri-, and hexavalency in the chromous salts, chromic salts, and chromates and dichromates respectively.

The methods employed for the accurate determination of the atomic weight of chromium have been concerned chiefly with the analysis of chromates and dichromates, notably those of silver, potassium, and ammonium. In the case of chromium, methods involving precipitation of a halogen from a solution of a halide are at a serious disadvantage owing to the difficulty of complete precipitation (see p. 26). The earliest work of importance was that of Berzelius,<sup>4</sup> who precipitated a known weight of lead nitrate as lead chromate, and deduced an atomic weight for chromium of about 56. This was high because the chromate precipitate carried down traces of alkali salts. Péligot, in 1844,<sup>5</sup> questioned this result, and from analyses of the chlorides and of chromous acetate gave the value 52.5, but did not support it with sufficient experimental data. Many other investigators<sup>6</sup> turned their attention to the subject, but most of the figures obtained are of no modern significance.<sup>7</sup> The most reliable value is that obtained by Baxter and his collaborators, whose experimental work was carried out with all the precautions which modern investigations have proved to be necessary.<sup>8</sup> The work consisted in the analysis of pure silver chromate<sup>9</sup> and of pure silver dichromate.<sup>10</sup> The weighed salt was dissolved in nitric acid and

<sup>1</sup> Kelley, *J. Amer. Electrochem. Soc.*, 1923, 43, 351.

<sup>2</sup> See Stiasny and Das, *J. Soc. Chem. Ind.*, 1912, 31, 753.

<sup>3</sup> Bock, *Chem. Zentr.*, 1904, ii., 1515; Koenig, *Landw. Jahrb.*, 1910, 39, 775; Hébert, *Compt. rend.*, 1907, 145, 337.

<sup>4</sup> Berzelius, *Pogg. Annalen*, 1820, 8, 22.

<sup>5</sup> Péligot, *Compt. rend.*, 1844, 19, 609, 734; 1845, 20, 1187; 21, 74.

<sup>6</sup> Berlin, *J. prakt. Chem.*, 1846, 37, 609; 38, 149; Jacquelin, *Compt. rend.*, 1847, 24, 679; Möberg, *J. prakt. Chem.*, 1848, 43, 114; Lefort, *ibid.*, 1850, 51, 261; Wildenstain, *ibid.*, 1853, 59, 27; Kessler, *Pogg. Annalen*, 1855, 95, 208; 1861, 113, 137; Siewert, *Zeitsch. ges. Naturwiss.*, 1861, 17, 530; Baubigny, *Compt. rend.*, 1884, 98, 146; Rawson, *Trans. Chem. Soc.*, 1880, 55, 213; Meinecke, *Annalen*, 1891, 261, 339.

<sup>7</sup> For a review of the work done on the Atomic Weight of chromium see Clarke, *A Recalculation of the Atomic Weights*, *Smithsonian Misc. Coll.*, 1910, 54, No. 3, p. 340. Also Baxter, Mueller, and Hines, *Chem. News*, 1909, 100, 181.

<sup>8</sup> See Volume I., Chapter VII.

<sup>9</sup> Baxter, Mueller, and Hines, *J. Amer. Chem. Soc.*, 1909, 31, 529; *Chem. News*, 1909, 100, 181, 189, 199.

<sup>10</sup> Baxter and Jesse, *J. Amer. Chem. Soc.*, 1909, 31, 541; *Chem. News*, 1909, 100, 213, 228.

reduced either by sulphurous acid or hydrazine sulphate. The silver was then precipitated by dilute hydrochloric or hydrobromic acid and the halide compound weighed. The mean results obtained <sup>1</sup> were:

From analysis of $\text{Ag}_2\text{CrO}_4$	. . . . .	Cr=52.008
$\text{Ag}_2\text{Cr}_2\text{O}_7$	. . . . .	Cr=52.018
Mean value 52.011.		

From a consideration of these determinations the atomic weight of chromium is fixed <sup>2</sup> by the International Committee (1925) as 52.01.

Chromium is a simple element without isotopes.<sup>3</sup>

### ALLOYS OF CHROMIUM

The most important alloys of chromium are those containing iron, cobalt, or nickel. With other metals, chromium only forms alloys with difficulty, if at all. For example, if bismuth <sup>4</sup> or cadmium <sup>5</sup> is heated with chromium in a magnesia crucible, the fused metals separate into two immiscible layers, while copper, silver, tin, and zinc <sup>5</sup> are only slightly miscible. Attempts have been made to prepare chromium bronze by the electrolysis of a mixed solution of chromium and copper salts,<sup>6</sup> but no alloy was obtained, the deposit of copper only containing a small quantity of unalloyed chromium, possibly in the form of hydroxide. Again, when metallic calcium is heated with chromic chloride, the latter is reduced to the metal, but no alloy is produced even when the temperature is maintained at 1000° C. for three hours.<sup>7</sup>

Aluminium forms an alloy which appears to have the composition  $\text{Cr}_3\text{Al}$ , with a melting-point rather higher than 1600° C. It is best prepared <sup>8</sup> by heating together aluminium, chromium sesquioxide, and potassium dichromate.

Antimony, when fused with chromium, forms mixtures which <sup>9</sup> yield two definite alloys, namely,  $\text{CrSb}$  and  $\text{CrSb}_2$ . The former is dark grey, brittle, melts about 1125° C., and is readily attacked by dilute acids; the latter is silvery white, brittle, more stable towards acids, but decomposes at temperatures below its melting-point, only being stable below 675° C.

Cobalt readily alloys with chromium and yields a series of products of great utility, the properties of which are enhanced by the presence of tungsten. The latter metal alloys in all proportions with chromium and cobalt, and causes increased hardness in the products.<sup>10</sup> An alloy containing 15 per cent. of chromium and 10 per cent. of tungsten is suitable for making cold chisels and woodworking tools, while if the proportion of tungsten is increased to 40 per cent., the alloy is hard

<sup>1</sup> Assuming the following fundamental values: Ag=107.880; O=16.000; Cl=35.467; Br=79.916.

<sup>2</sup> For theoretical considerations, and discussion on methods of determining the atomic weight from observed data, see Vol. I.

<sup>3</sup> Aston, *Chemistry and Industry*, 1923, 42, 935.

<sup>4</sup> Williams, *Zeitsch. anorg. Chem.*, 1907, 55, 1.

<sup>5</sup> Hindrichs, *ibid.*, 1908, 59, 414.

<sup>6</sup> Kremann, Lorber, and Maas, *Monatsh.*, 1914, 35, 581.

<sup>7</sup> Hackspill, *Bull. Soc. chim.*, 1907, [4], 1, 895.

<sup>8</sup> Hindrichs, *loc. cit.*; Sisoo and Whitmore, *J. Ind. Eng. Chem.*, 1925, 17, 956.

<sup>9</sup> Williams, *loc. cit.*

<sup>10</sup> Haynes, *J. Ind. Eng. Chem.*, 1913, 5, 180.

enough to scratch quartz and can be used for turning cast iron. The addition of molybdenum also causes increased hardness. *Stellite* is an alloy of cobalt with 25 per cent. of chromium, and containing tungsten and molybdenum.<sup>1</sup> It is used for making high-speed tools, since it takes a good cutting edge which it retains at temperatures above red heat, and such tools can be used for a long time without grinding. It is "rustless" to a high degree and is not attacked by organic or nitric acids. The presence of carbon, silicon, or boron in these alloys renders them harder but more brittle.

Iron-chromium alloys, free from carbon, may be prepared from chromite by the alumino-thermic method. From a study of the cooling- and freezing-point curves it has been suggested that a compound,  $\text{Cr}_2\text{Fe}$ , exists,<sup>2</sup> but this is questioned by Jänecke,<sup>3</sup> who studied the iron-chromium system by means of fusion curves and by the microscopic study of polished sections of various alloys between the limits 10 Fe : 90 Cr and 90 Fe : 10 Cr, and came to the conclusion that the system consists of a single eutectic which can form mixed crystals with either component. The eutectic contains 75 per cent. of chromium and melts at  $1320^\circ\text{C}$ . The addition of chromium to iron increases the readiness of attack by hydrochloric and sulphuric acids, but towards concentrated nitric acid the alloys are rendered passive. They remain bright in air and in water. The presence of carbon increases the resistance to acids and renders them very hard; if carbon-free, they are softer than cast iron. All the alloys up to 80 per cent. chromium are magnetic. Molybdenum, titanium, vanadium, and tungsten improve the mechanical properties and increase the resistance to acids.

The chief use of ferro-chrome alloys is in the manufacture of chromium steels, *i.e.* steels containing about 2 per cent. of chromium;<sup>4</sup> the alloys, containing over 60 per cent. of chromium, are added to ordinary carbon steel when molten. Chromium steels are very hard and tough. The so-called "stainless" or "rustless" steels usually contain 13 to 14 per cent. chromium, with occasionally 1 per cent. nickel.<sup>5</sup> The mechanical relations of iron, chromium, and carbon, and the structure of chromium steels are subjects which have been exhaustively studied.<sup>6</sup>

Nickel readily alloys with chromium and iron. *Nichrome*, containing 60 per cent. nickel, 14 per cent. chromium, and 15 per cent. iron,<sup>7</sup> is a high-temperature resisting alloy with a much longer life than ordinary iron or steel. It is used for making annealing and carbonising boxes, retorts for use at high temperatures, and for pyrometer tube covers. Nickel-chromium steels are of great importance and have been largely used for the manufacture of big guns.<sup>8</sup>

<sup>1</sup> Haynes, *Mining Mag.*, December 1917, p. 393.

<sup>2</sup> Moenart, *Metallurgie*, 1911, 8, 101, 193; Treitschko and Tammann, *Zeitsch. anorg. Chem.*, 1907, 55, 402.

<sup>3</sup> Jänecke, *Zeitsch. Elektrochem.*, 1917, 23, 49.

<sup>4</sup> See Vol. IX., Part III., of this series.

<sup>5</sup> Rumbold, *Chromium Ore*, Monograph on Mineral Resources, Imperial Inst., 1921.

<sup>6</sup> See Arnold and Read, *J. Iron Steel Inst.*, 1911, 83, 249; Edwards, Greenwood, and Kikkawa, *ibid.*, 1916, 93, 114; Portevin, *Compt. rend.*, 1911, 153, 64; Guillet, *ibid.*, 1904, 139, 426; Giolitti and Carnevali, *Atti R. Acad. Sci. Torino*, 1911, 46, 568.

<sup>7</sup> Griffiths, *J. Iron Steel Inst.*, 1917, 96, 449.

<sup>8</sup> For an account of these steels see Vol. IX., Part III., of this series. Also see Guillet, on the structure of nickel chromium steels, *Compt. rend.*, 1913, 156, 1774; 1914, 158, 412.

Chromium-vanadium steel is an alloy steel combining high tensile strength and resistance to shock.<sup>1</sup>

**Chromium Amalgams.**—An amalgam of composition  $\text{Hg}_3\text{Cr}$  may be prepared <sup>2</sup> by the electrolysis of a solution of chromic chloride in dilute hydrochloric acid with a powerful current, the cathode being of mercury and the anode of platinum. The amalgam is solid, soft, brilliant, and only slightly acted on by air. When heated, it loses mercury without melting and oxidises rapidly. When subjected to a pressure of 200 kilos. per sq. cm., it loses mercury and yields another amalgam of composition  $\text{HgCr}$ . This is brilliant, harder than the first, and more readily changes in air. Both decompose on distilling in a vacuum below  $300^\circ \text{C}$ ., yielding chromium which is pyrophoric at ordinary temperatures.

<sup>1</sup> See Harbord and Hall, *The Metallurgy of Steel* (Griffin, 1911), p. 414.

<sup>2</sup> Férée, *Compt. rend.*, 1895, 121, 822.

## CHAPTER III.

### CHROMIUM COMPOUNDS.

#### GENERAL PROPERTIES OF CHROMIUM COMPOUNDS.

THE chemistry of chromium is somewhat complicated owing to the varying degrees of valency exhibited by the element. In its three most important oxides, all of which give rise to corresponding series of salts, it functions respectively as a di-, tri-, and hexa-valent element, while in some of its compounds it behaves as a hepta-, penta-, or even tetra-valent element.

The oxide  $\text{CrO}$ , chromous oxide, containing divalent chromium, is strongly basic and gives rise to the chromous salts, for example, chromous chloride,  $\text{CrCl}_2$ , which are similar in character to the ferrous and manganous salts except that they show a greater tendency to become oxidised by the air, or other oxidising agents, to the chromic condition. They therefore act as powerful reducers. The analogy to iron and manganese, and also to vanadium, its congener in Group V. (see frontispiece), is further shown in the sulphate,  $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ , and its double salts. The stability of these isomorphous sulphates increases in the order  $\text{V} - \text{Cr} - \text{Mn}$ .

The sesquioxide,  $\text{Cr}_2\text{O}_3$ , containing trivalent chromium, is an amphoteric oxide. It yields chromic salts, such as chromic chloride,  $\text{CrCl}_3$ , and sulphate,  $\text{Cr}_2(\text{SO}_4)_3$ , which are very stable and show great similarity to the ferric salts and to salts of aluminium as, for example, in the formation of alums. Since, however, chromic oxide functions as a weaker base than chromous oxide, the latter having a lower oxygen content, the chromic salts are more liable to hydrolysis than the chromous salts. This is well marked in the case of the chlorides. Again, in spite of the stability of chromic salts, only a slight tendency to form simple  $\text{Cr}^{+++}$  ions is exhibited, whilst complex ions are formed much more readily, not only complex anions, as in the case of iron and aluminium, but also complex cations, as in the extensive chromamine series.<sup>1</sup> In this respect chromium resembles cobalt and platinum.

An interesting form of isomerism, dependent on the formation of such cations, is exhibited by chromic salts; which usually exist in at least two modifications, the one green and the other violet or dark blue. In both varieties the chromium is in the same state of oxidation, but the non-metallic radicle, while apparently freely ionised in a violet solution, is only partly active in the green. Thus the chlorine in violet chromic chloride,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , is completely precipitated by the addition of a soluble silver salt, but in the ordinary green variety only one-third of

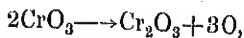
<sup>1</sup> See Vol. X. of this series.

the chlorine can be so precipitated; a third isomeride, green in colour, in which two-thirds of the chlorine can be precipitated, is also known. The probable constitution of these isomers is discussed later under the respective compounds. In a solution of a chromic salt equilibrium is gradually set up between the violet and green varieties, the proportion of each present depending on the temperature and the total concentration. The violet solutions on heating usually turn green, the violet form of the salt being less stable at higher temperatures. The formation of the green variety is also favoured by concentration. Nevertheless, evaporation of a green solution generally leads to the formation of a basic salt due to hydrolysis. The less soluble violet salts are therefore more readily obtained in the crystalline form than are the green. The rate at which equilibrium sets up varies with different salts. Solutions of the chloride, nitrate, and acetate readily become green when heated to 95° C., and return to violet on cooling; the sulphate, however, changes much more slowly.<sup>1</sup> Owing to the difference in the constitution of the two types of compounds, and its effect on the nature of their ionisation, solutions of the violet salts have different electrical conductivity from that of solutions of the corresponding green salts of the same concentration, and use has been made of this fact in determining the rate of change. The two modifications also act as hydrolytic catalysts showing distinct differences in their degree of activity.<sup>1</sup>

Chromic oxide also exhibits acidic properties, combining with strong bases to form chromites.

Chromium trioxide,  $\text{CrO}_3$ , or chromic anhydride, is a strong acid-forming oxide, producing chromic acid and the chromates analogous to sulphuric acid and the sulphates. The position of chromium as the first member of the A subgroup of Group VI. of the Periodic Table explains the extreme stability of this oxide and its derivatives, in which the metal figures as a hexavalent element. There is a far-reaching analogy between these compounds and the corresponding compounds of the other members of the group, as may be seen, for example, in the isomorphism of the sulphates, chromates, selenates, molybdates, and tungstates. The closer relation between chromium, molybdenum, and tungsten shows itself in the formation of condensed poly-acids, whereas similar compounds of sulphuric acid are not known.

Chromium trioxide and the salts of chromic acid are powerful oxidising agents. The action depends upon the reduction of chromium to the trivalent condition thus:

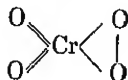


so that chromic compounds result, and the reaction is accompanied by a colour change from yellow to green.

It is thought by some that the metal acts as a tetravalent element in chromium dioxide,  $\text{CrO}_2$ , but this compound may also be considered as a basic chromic chromate,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ . Chromium appears to function as a pentavalent element in the oxychloride,  $\text{CrOCl}_3$ , and its derivatives. The perchromic acids and perchromates have long been thought to contain heptavalent chromium, but it would appear that

<sup>1</sup> Whitney, *Zeitsch. physikal. Chem.*, 1896, 20, 40; cf. Recoura, *Compt. rend.*, 1890, 110, 1029.

some of these compounds at least are derived from a hypothetical chromium tetroxide,  $\text{CrO}_4$ , in which the element is hexavalent, thus :



These compounds are extremely unstable.

#### CHROMIUM AND HYDROGEN.

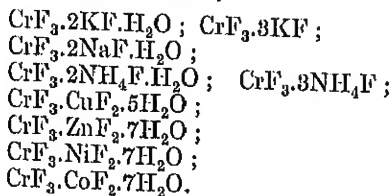
No definite compound of chromium and hydrogen has been prepared, though the electrolytically deposited metal occludes the gas to the extent of 250 times its own volume.<sup>1</sup>

#### CHROMIUM AND FLUORINE.

**Chromous Fluoride**,  $\text{CrF}_2$ , results<sup>2</sup> as a green crystalline solid, fusible at  $1100^\circ \text{C}$ . and of density 4.11, from the action of hydrogen fluoride on chromium at a red heat.

**Chromic Fluoride**,  $\text{CrF}_3$ , is obtained in the anhydrous condition either by passing hydrogen fluoride over heated chromic chloride,<sup>3</sup> or by strongly heating a mixture of dried (but not ignited) chromic oxide and aqueous hydrofluoric acid.<sup>3</sup> It is a green substance, of density 3.78, which melts at  $1100^\circ \text{C}$ . and sublimes at  $1200^\circ \text{C}$ . Several hydrates are known. The *heptahydrate*,  $\text{CrF}_3 \cdot 7\text{H}_2\text{O}$ , which crystallises in green prisms, may be prepared by treating an aqueous solution of the anhydrous salt with alcohol.<sup>2</sup> The *tetrahydrate*,  $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ , which may be used as a mordant, can be obtained from a solution of chromic hydroxide in hydrofluoric acid.<sup>4</sup> By addition of ammonium fluoride to a cold solution of chromic sulphate, the slightly soluble crystalline *nonahydrate*,  $\text{CrF}_3 \cdot 9\text{H}_2\text{O}$ , results.<sup>5</sup> In hydrochloric acid it yields a violet, and in potash a green, solution. On heating in the air it decomposes, leaving a residue of chromium sesquioxide,  $\text{Cr}_2\text{O}_3$ . The hydrates,  $\text{CrF}_3 \cdot 6\text{H}_2\text{O}$ ,  $2\text{CrF}_3 \cdot 7\text{H}_2\text{O}$ , and  $\text{CrF}_3 \cdot 8\text{H}_2\text{O}$ , have been described,<sup>6</sup> as also have complex fluorides of chromium and pyridine.<sup>7</sup>

Double fluorides with the alkali metals, ammonium, copper, zinc, nickel, and cobalt, are known, namely :<sup>8</sup>



<sup>1</sup> Carveth and Curry, *J. Physical Chem.*, 1905, 9, 353.

<sup>2</sup> Poulenc, *Compt. rend.*, 1893, 116, 253 ; *Ann. Chim. Phys.*, 1894, [7], 2, 5.

<sup>3</sup> Deville, *Compt. rend.*, 1856, 43, 970.

<sup>4</sup> Koeppe, *Chem. Zentr.*, 1888, p. 1432.

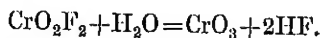
<sup>5</sup> Fabris, *Gazzetta*, 1890, 20, 582.

<sup>6</sup> Werner and Costăchescu, *Ber.*, 1908, 41, 4242 ; Recoura, *Compt. rend.*, 1913, 157, 1525.

<sup>7</sup> Costăchescu, *Ann. Sci. Univ. Jassy*, 1912, 7, 87 ; 1914, 8, 10.

<sup>8</sup> Christensen, *J. prakt. Chem.*, 1887, [2], 35, 161 ; Wagner, *Ber.*, 1888, 19, 890 ; Potorson, *J. prakt. Chem.*, 1889, [2], 40, 52 ; Higley, *J. Amer. Chem. Soc.*, 1904, 26, 613.

**Chromyl Fluoride**,  $\text{CrO}_2\text{F}_2$ , was obtained by Unverdorben<sup>1</sup> who, on heating a mixture of fluorspar and lead chromate with fuming sulphuric acid, observed the formation of a red gas, originally believed to be a higher fluoride of chromium, namely,  $\text{CrF}_6$  or  $\text{CrF}_{10}$ . Dumas,<sup>2</sup> by cooling the gas, obtained it as a liquid. It is a blood-red liquid,<sup>3</sup> decomposed by water, with the formation of chromium trioxide and hydrogen fluoride,



It acts on glass, forming silicon tetrafluoride, and with ammonium chromate, a fluo-chromate is formed.<sup>4</sup>

**Chromium Silico-fluoride**,  $\text{Cr}_2\text{F}_6 \cdot (\text{SiF}_4)_3$ , is known in solution (see p. 102).

#### CHROMIUM AND CHLORINE.

**Chromous Chloride**,  $\text{CrCl}_2$ , may be prepared in the anhydrous condition by heating chromic chloride,  $\text{CrCl}_3$ , to incipient redness in a current of dry hydrogen quite free from oxygen,<sup>5</sup> or at a high temperature in ammonium chloride vapour;<sup>6</sup> by passing hydrogen chloride over chromium at a red heat;<sup>7</sup> and, together with chromic chloride, by the action of chlorine on a mixture of chromium sesquioxide and carbon.<sup>8</sup> Anhydrous chromous chloride can also be obtained by carefully heating the hydrated salt at  $250^\circ \text{C}$ . in a current of nitrogen.<sup>9</sup> It forms white lustrous hygroscopic needles of density 2.751 at  $14^\circ \text{C}$ .,<sup>10</sup> stable in dry air. It volatilises with difficulty at a high temperature, the vapour density diminishing with rise in temperature, thus:<sup>11</sup>

Temperature, ° C.	Vapour Density (Air=1).
1300-1400	7.800
1400-1500	7.278
1500-1600	6.244

The theoretical vapour density corresponding to the formula  $\text{CrCl}_2$  is 4.256.

The salt is soluble in water, yielding a blue solution which may be used as a reducing agent,<sup>12</sup> since it absorbs oxygen, even from the air,

<sup>1</sup> Unverdorben, *Trommsd. N.J. Pharm.*, 1824, 9, 1, 20; *Pogg. Annalen*, 1820, 7, 311.

<sup>2</sup> Dumas, *Ann. Chim. Phys.*, 1826, [2], 31, 436.

<sup>3</sup> Olivieri, *Gazzetta*, 1880, 16, 218.

<sup>4</sup> See p. 47; also Evans, *Zeitsch. angew. Chem.*, 1891, 4, 18; Rose, *Pogg. Annalen*, 1833, 27, 565.

<sup>5</sup> Moberg, *J. prakt. Chem.*, 1843, 29, 175; 1848, 44, 322; Péligot, *Ann. Chim. Phys.*, 1844, [3], 12, 528; Berzelius, *Öfvers. K. Vet. Akad. Forh.*, 1844, p. 204; Forbes and Richter, *J. Amer. Chem. Soc.*, 1917, 39, 1140.

<sup>6</sup> Moissan, *Compt. rend.*, 1881, 92, 702.

<sup>7</sup> Ufer, *Annalen*, 1859, 112, 302; Moissan, *loc. cit.*; Koppel, *Zeitsch. anorg. Chem.*, 1905, 45, 359.

<sup>8</sup> Péligot, *loc. cit.*

<sup>9</sup> Recoura, *Ann. Chim. Phys.*, 1887, [6], 10, 1.

<sup>10</sup> Grabfield, *Amer. Chem. J.*, 1883, 5, 240.

<sup>11</sup> Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, 53, 828; *Compt. rend.*, 1888, 107, 529.

<sup>12</sup> Chesneau, *Compt. rend.*, 1889, 129, 100; Kohlschütter, *Ber.*, 1904, 37, 3053; Moissan, *loc. cit.*; Péligot, *loc. cit.*

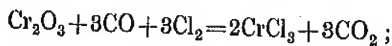


with production of an oxychloride,  $\text{Cr}_2\text{Cl}_4\text{O}$ .<sup>1</sup> For this reason it has been proposed for use in gas analysis, but it is not a trustworthy reagent, the absorption of oxygen not being complete.<sup>2</sup> The solution can readily be obtained by reduction, in absence of air, of a solution of chromic chloride, or of a mixture of potassium dichromate solution and fuming hydrochloric acid, by means of zinc;<sup>3</sup> or, together with chromic chloride, by the electrolysis of a solution of potassium chloride, using a chromium anode.<sup>4</sup>

With alkali hydroxide a solution of chromous chloride yields a yellowish-brown precipitate which absorbs oxygen, forming a hydrated chromo-chromic oxide,<sup>5</sup>  $\text{Cr}_3\text{O}_4 \cdot \text{H}_2\text{O}$ .

The *tetrahydrate*,  $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ , is formed when chromous chloride solution is rapidly evaporated to dryness below  $50^\circ \text{C}$ . in a vacuum.<sup>6</sup> The hydrate is capable of existing in two distinct modifications, namely, as dark blue and dark green needles respectively, the solution being green when hot, concentrated, and acidulated, or blue if cold and dilute.<sup>7</sup> The *tri-* and *di-hydrates*,  $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$  and  $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$ , also exist,<sup>8</sup> the former as pale blue crystals and the latter in a light green amorphous condition. A *hexahydrate*,  $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$ , has also been described, but its existence has not been confirmed.<sup>9</sup> In solution, chromous chloride is catalytically decomposed by platinum.<sup>10</sup> A *hydrochloride*,  $3\text{CrCl}_2 \cdot 2\text{HCl} \cdot 18\text{H}_2\text{O}$ , is formed on passing hydrogen chloride free from oxygen into a concentrated solution of the salt.<sup>11</sup> It is a fine powder, unstable at  $20^\circ \text{C}$ .

**Chromic Chloride,  $\text{CrCl}_3$ .**—The anhydrous salt may be obtained by a variety of methods, for example, (1) by heating metallic chromium at  $600^\circ \text{C}$ . in a stream of chlorine;<sup>12</sup> (2) by passing a stream of chlorine<sup>13</sup> over chromium sesquioxide at  $440^\circ \text{C}$ .; (3) by heating a mixture of the sesquioxide and carbon in a stream of chlorine;<sup>14</sup> (4) by the action of a mixture of carbon monoxide and chlorine on chromium sesquioxide at a red heat;<sup>15</sup>



(5) by the interaction<sup>16</sup> of phosphorus trichloride and chromyl chloride,  $\text{CrO}_2\text{Cl}_2$  (see p. 91); or of chromyl chloride, carbon monoxide, and

<sup>1</sup> Péligot, *loc. cit.*; Löwel, *Ann. Chim. Phys.*, 1854, [3], 40, 45; Manchot and Herzog, *Ber.*, 1900, 33, 1742.

<sup>2</sup> Anderson and Riffe, *J. Ind. Eng. Chem.*, 1916, 8, 24.

<sup>3</sup> Moissan, *Ann. Chim. Phys.*, 1882, [6], 25, 401; Anderson and Riffe, *loc. cit.*

<sup>4</sup> Kuessner, *Zeitsch. Elektrochem.*, 1910, 16, 764.

<sup>5</sup> Péligot, *Compt. rend.*, 1844, 19, 608, 734.

<sup>6</sup> Knight and Rich, *Trans. Chem. Soc.*, 1911, 99, 87.

<sup>7</sup> Moissan, *loc. cit.*; von der Pfordten, *Annalen*, 1886, 228, 112; Recoura, *Ann. Chim. Phys.*, 1887, [6], 10, 10; Prudhomme, *Bull. Soc. ind. Mulhouse*, 1889, 59, 603; Molbain, *Disseration*, Heidelberg; Rich, *Proc. Chem. Soc.*, 1908, 24, 215; Knight and Rich, *Trans. Chem. Soc.*, 1911, 94, 87. See also Koppel, *Zeitsch. anorg. Chem.*, 1905, 45, 359; Hittorf, *Zeitsch. physikal. Chem.*, 1898, 25, 729; 1899, 30, 481; Ostwald, *ibid.*, 1900, 35, 33, 204; Brauer, *ibid.*, 1901, 38, 441; Döring, *J. prakt. Chem.*, 1902, [2], 66, 66; 1906, [2], 73, 392; Mazzucchelli, *Gazzetta*, 1905, 35, [1], 417.

<sup>8</sup> Knight and Rich, *loc. cit.*

<sup>9</sup> Moissan, *Ann. Chim. Phys.*, 1882, [6], 25, 401.

<sup>10</sup> Jablęzyński, *Bull. Acad. Sci. Cracow*, 1908, p. 398.

<sup>11</sup> Recoura, *Compt. rend.*, 1885, 100, 1227; Prudhomme, *loc. cit.*

<sup>12</sup> Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 449; *Bull. Soc. chim.*, 1872, [2], 17, 205.

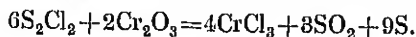
<sup>13</sup> Moissan, *Ann. Chim. Phys.*, 1882, [6], 25, 401; *Compt. rend.*, 1881, 92, 1051.

<sup>14</sup> Wöhler, *Annalen*, 1850, 111, 233.

<sup>15</sup> Quantin, *Compt. rend.*, 1884, 99, 707; 1887, 104, 223.

<sup>16</sup> Michaelis, *loc. cit.*

chlorine.<sup>1</sup> (6) Undoubtedly the most convenient method is that of Bourion,<sup>2</sup> who finds that sulphur chloride alone is preferable to a mixture of that substance with chlorine for the chlorination of the oxide. Precipitated calcined chromic oxide is attacked by sulphur chloride at a temperature rather above 400° C., but below red heat :



Modifications of the foregoing and other methods have been suggested.<sup>3</sup>

Anhydrous chromic chloride forms large, lustrous, unctuous plates of the colour of peach blossom, of density<sup>4</sup> 2.757 at 15° C. It has a specific heat of 0.143.<sup>5</sup> Its vapour density just above 1065° C., at which temperature it volatilises, is 6.135 (air=1), whilst at 1200° C. it approximates to the theoretical value, 5.478, required by the formula  $\text{CrCl}_3$ . At much higher temperatures partial decomposition takes place, with consequent diminution of the vapour density.<sup>6</sup>

Chromic chloride is reduced at a red heat by hydrogen to chromous chloride, and by zinc or magnesium to metallic chromium. Heated in air, green chromium sesquioxide is formed; in oxygen or moist chlorine, chromyl chloride is produced.<sup>7</sup> On strongly heating in dry ammonia, the nitride,  $\text{CrN}$ , is obtained, whilst in presence of ammonium chloride, the lower chloride is formed; in hydrogen sulphide, the black crystalline sesquisulphide  $\text{Cr}_2\text{S}_3$ , and with phosphorous pentachloride, the double chloride  $2\text{CrCl}_3 \cdot \text{PCl}_5$ , are produced.<sup>8</sup> Mineral acids, including even aqua regia, have no action on the anhydrous salt; fused alkali hydroxide or carbonate, in presence of nitrate, yields alkali chromate and chloride. Anhydrous chromic chloride is almost insoluble in cold water, but dissolves readily in presence of very slight traces (0.00001 per cent.) of chromous chloride, either previously added or formed in solution by the addition of a reducing agent such as tin, zinc, ferrous or cuprous chlorides.<sup>9</sup> It has not been proved that the catalytic influence of these reagents is wholly due to the formation of chromous chloride. Chromic chloride is sparingly soluble in boiling water.<sup>10</sup>

A solution of chromic chloride is readily obtained by the action of dilute hydrochloric acid on chromic hydroxide, or on chromium sesquioxide which has not been ignited; this solution on evaporation yields an amorphous, deliquescent, green mass, soluble in water and in alcohol.<sup>11</sup> The product on heating in hydrogen chloride or chlorine at temperatures above 250° C. becomes anhydrous, at the same time assuming the usual colour of the anhydrous salt. Basic chlorides are formed by

<sup>1</sup> Demarcay, *Compt. rend.*, 1887, 104, 111.

<sup>2</sup> Bourion, *Ann. Chim. Phys.*, 1910, [8], 21, 50.

<sup>3</sup> Ufer, *Annalen*, 1859, 112, 284; Fellenberg, *Pogg. Annalen*, 1840, 50, 70; Brunner, *Dingl. poly. J.*, 1861, 159, 356; Curie, *Chem. News*, 1873, 28, 307; de Claubry, *Ann. Chim. Phys.*, 1830, 45, 110; Vosmaer, *Zeitsch. anal. Chem.*, 1889, 28, 324; Matignon and Bourion, *Compt. rend.*, 1904, 138, 760; Mourel, *Anal. Fis. Quim.*, 1910, 8, 196.

<sup>4</sup> Grabfield, *Amer. Chem. J.*, 1883, 5, 240; Clarke, *J. Amer. Chem. Soc.*, 1892, [3], 14, 281, gives density at 17.2° C. = 2.357.

<sup>5</sup> Kopp, *Annalen*, 1864, 3, 294.

<sup>6</sup> Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, 53, 828; *Compt. rend.*, 1888, 107, 529.

<sup>7</sup> Moissan, *loc. cit.*

<sup>8</sup> Cronander, *Ber.*, 1873, 6, 1466; Barreswill, *J. Pharm.*, 1844, [3], 4, 455; Löwel, *ibid.*, 1845, [3], 7, 424; Recoura, *Compt. rend.*, 1886, 102, 923; Bunge, *Chem. Zentr.*, 1866, p. 258; Rohland, *Zeitsch. anorg. Chem.*, 1901, 29, 159.

<sup>9</sup> Drucker, *Zeitsch. physikal. Chem.*, 1901, 36, 173; Rohland, *Zeitsch. anorg. Chem.*, 1899, 21, 37; 1901, 29, 159; Polouzo, *Ann. Chim. Phys.*, 1845, [3], 14, 251; Pélégot, *ibid.*, 1844, 12, 533; 1845, 14, 240.

<sup>10</sup> Jacquelin, *Compt. rend.*, 1847, 24, 679.

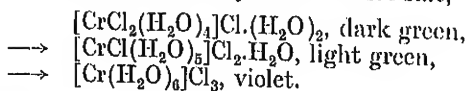
<sup>11</sup> Pélégot, *Ann. Chim. Phys.*, 1844, [3], 12, 537; Recoura, *Compt. rend.*, 1886, 102, 515.

heating the hydrated chloride in air.<sup>1</sup> A number of hydrates, one at least appearing to exist in three isomeric forms, have been prepared. The hydrates in solution all yield the same hydroxide,  $\text{Cr}(\text{OH})_3$ , on treatment with an alkali hydroxide.

Dilute solutions of the chloride are violet in colour, while more concentrated or acidulated solutions are green, the colour depending on the equilibrium established between the green and violet modifications of the salt<sup>2</sup> which is in solution as the *hexahydrate*,<sup>3</sup>  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . The amount of the green salt present at equilibrium increases with concentration. The violet modification is precipitated before the green when hydrogen chloride is passed into a boiled solution of the mixture. From dehydration experiments Werner concluded that the molecule of the green hydrate contained  $4\text{H}_2\text{O}$  as water of constitution and  $2\text{H}_2\text{O}$  as water of crystallisation, while the violet modification contained  $6\text{H}_2\text{O}$  as water of constitution. Olie confirmed these results at ordinary temperatures, but found that at  $100^\circ \text{C}$ . both varieties lost approximately  $4\text{H}_2\text{O}$ . Further, Werner found that from solutions of the violet hydrate, the whole, and from solutions of the green hydrate only one-third, of the chlorine could be precipitated by a soluble silver salt. Although the amount of chlorine precipitated appears to depend to a certain extent on the conditions of the experiment, yet it is evident that in the two salts the chlorine is not all similarly combined. The isomerism was explained by Werner according to the co-ordination theory,<sup>4</sup> and the violet and green chlorides were considered to possess the formulæ  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  and  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot (\text{H}_2\text{O})_2$  respectively, the former being termed the hexaquo salt and the latter dichlorotetraquo-chromic chloride, or simply dichlorochromium chloride.<sup>5</sup>

It has been suggested<sup>6</sup> that the greyish-blue or violet chromic chloride is bimolecular,  $2[\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3]$ , while the green variety is unimolecular. This is not accepted by Bjerrum,<sup>7</sup> who considered that, in order to interpret the equilibrium changes of a concentrated solution of chromic chloride, it was necessary to assume the presence of a third isomeric hexahydrate in the solution. This he succeeded in isolating, as very deliquescent pale green crystals, by adding ether saturated with hydrogen chloride to the solution remaining after precipitating the violet salt with hydrogen chloride. Two-thirds of the chlorine present in this compound may be precipitated by means of silver nitrate, so that it may be regarded as monochloropentaquochromic chloride,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ .

In dilute solution the dark green hexahydrate changes rapidly to the light green salt, and then more slowly to the violet salt,<sup>8</sup> thus :



<sup>1</sup> Berzelius, *Traité de chimie*, 4, 400; Péligot, *loc. cit.*

<sup>2</sup> Roozboom, *Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 66; Olie, *Zeitsch. anorg. Chem.*, 1906, 51, 29.

<sup>3</sup> Marchetti, *Gazzetta*, 1882, 22, 375.

<sup>4</sup> Olie, *Zeitsch. anorg. Chem.*, 1907, 52, 48, 62; Werner and Gubser, *Ber.*, 1901, 34, 1570; Weinland and Koch, *Zeitsch. anorg. Chem.*, 1904, 39, 206; Bjerrum, *Ber.*, 1906, 39, 1597; Higley, *J. Amer. Chem. Soc.*, 1904, 26, 613; Jost, *Ber.*, 1906, 39, 4327.

<sup>5</sup> Sand and Gramling, *Zeitsch. physikal. Chem.*, 1908, 62, 1, 28.

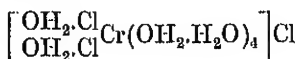
<sup>6</sup> Bjerrum, *ibid.*, 1910, 73, 724; 1907, 59, 581.

<sup>7</sup> Heydweiller, *Zeitsch. anorg. Chem.*, 1915, 91, 66.

<sup>8</sup> See Vol. X.

The influence of light <sup>1</sup> and of the presence of neutral chlorides <sup>2</sup> on the transformation has been studied.<sup>3</sup>

By dehydration of the green hydrate, Bjerrum <sup>4</sup> obtained two red substances,  $2\text{CrCl}_3 \cdot 3\text{H}_2\text{O}$  and  $2\text{CrCl}_3 \cdot \text{H}_2\text{O}$ . Other hydrates are the *decahydrate*,  $\text{CrCl}_3 \cdot 10\text{H}_2\text{O}$ , and *tetrahydrate*,  $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$ . The former yields <sup>5</sup> brilliant green triclinic crystals, strongly dichroic, and can be obtained by triturating the hexahydrate with the calculated amount of water.<sup>6</sup> Werner and Gubser <sup>7</sup> assign the formula



to the decahydrate, which in dry air loses water, being converted first into the hexahydrate and finally into the tetrahydrate, a pale green, slightly hygroscopic powder.<sup>8</sup> A hydrate,  $2\text{CrCl}_3 \cdot 9\text{H}_2\text{O}$ , has also been said to exist.<sup>9</sup> An alcoholate,  $\text{CrCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$ , in the form of red needles, stable in dry air, has been obtained by the action of dry hydrogen chloride in absolute alcohol upon metallic chromium.<sup>10</sup> Double salts with alkali chlorides,<sup>11</sup> with antimony pentachloride,<sup>12</sup> with organic bases,<sup>13</sup> ammonia (for example,  $2\text{CrCl}_3 \cdot 12\text{NH}_3 \cdot 2\text{H}_2\text{O}$  and  $2\text{CrCl}_3 \cdot 10\text{NH}_3$ ), and substituted ammonias<sup>14</sup> are known. Complex halogen-halides (see p. 81 and chlorosulphates (see p. 83) have also been obtained.

On progressive hydrolysis, chromic chloride gives rise <sup>15</sup> to two soluble basic chlorides,  $\text{Cr}(\text{OH})\text{Cl}_2$  and  $\text{Cr}(\text{OH})_2\text{Cl}$ , and an insoluble grey-green hydroxide. The compound,  $\text{Cr}(\text{OH})_2\text{Cl}$ , is never present in any large proportion, and the hydroxide is only formed upon addition of alkali. The formulae of the three compounds are probably  $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]\text{Cl}_2$ ,  $[\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2]\text{Cl}$ , and  $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$  respectively.

**Oxychlorides.**—Several oxychlorides of chromium said <sup>16</sup> to possess definite formulae, for example,  $\text{Cr}_2\text{Cl}_5\text{O} \cdot 4\text{H}_2\text{O}$ ,  $\text{Cr}_2\text{Cl}_4(\text{OH})_2$ ,  $\text{Cr}_2\text{Cl}_4 \cdot \text{Cr}_2\text{O}_3$ ,  $\text{Cr}_2\text{Cl}_2(\text{OH})_4$ ,  $\text{Cr}_2\text{Cl}(\text{OH})_5$ ,  $\text{Cr}_2\text{O}_3 \cdot 8\text{CrCl}_3 \cdot 24\text{H}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3 \cdot 4\text{CrCl}_3 \cdot 9\text{H}_2\text{O}$ ,  $2\text{Cr}_2\text{O}_3 \cdot 2\text{CrCl}_3$ , and  $\text{CrOCl} \cdot 8\text{H}_2\text{O}$ , have been described, but possibly some of them are merely physical mixtures. Basic chromium

<sup>1</sup> Kurilov, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 469; *Kolloid. Zeitsch.*, 1914, 14, 171.

<sup>2</sup> Baldwin, *J. Amer. Leather Chem. Assoc.*, 1919, 14, 10.

<sup>3</sup> For density and electrical conductivity determinations, see Heydweiller, *loc. cit.*; Hopfgartner, *Monatsh.*, 1910, 40, 259.

<sup>4</sup> Bjerrum, *Ber.*, 1907, 40, 2915.

<sup>5</sup> Godefroy, *Bull. Soc. chim.*, 1885, [2], 43, 229.

<sup>6</sup> Olie, *Zeitsch. anorg. Chem.*, 1907, 53, 268.

<sup>7</sup> Werner and Gubser, *Ber.*, 1906, 39, 1823.

<sup>8</sup> Godefroy, *Compt. rend.*, 1885, 100, 105.

<sup>9</sup> See also Löwel, *Ann. Chim. Phys.*, 1845, [3], 14, 246; 1854, 40, 43; Sénarmont, *Compt. rend.*, 1851, 32, 702; Foytis, *ibid.*, 1913, 156, 886.

<sup>10</sup> Koppel, *Zeitsch. anorg. Chem.*, 1901, 28, 461.

<sup>11</sup> Werner and Gubser, *Ber.*, 1906, 39, 1823; Weinland and Schumann, *ibid.*, 1907, 40, 3767; Bjerrum and Hansen, *Zeitsch. anorg. Chem.*, 1909, 63, 151.

<sup>12</sup> Pfeiffer, *Zeitsch. anorg. Chem.*, 1903, 36, 349.

<sup>13</sup> Pfeiffer, *ibid.*, 1907, 55, 97; Bennett and Turner, *Trans. Chem. Soc.*, 1914, 105, 1057.

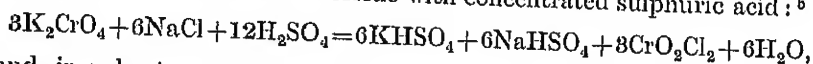
<sup>14</sup> Lang and Joliffe, *Proc. Chem. Soc.*, 1903, 19, 147; Lang and Carson, *ibid.*, 1903, 19, 147; *J. Amer. Chem. Soc.*, 1904, 26, 758.

<sup>15</sup> Bjerrum, *Zeitsch. physikal. Chem.*, 1910, 73, 724.

<sup>16</sup> Schiff, *Annalen*, 1862, 124, 157; Klotzinsky, *Zeitsch. Chem.*, 1866, p. 127; Aberg, *J. prakt. Chem.*, 1843, 29, 175; Löwel, *ibid.*, 1846, 37, 38; Pélégot, *ibid.*, 1846, 37, 475; Ordway, *Amer. J. Sci.*, 1858, [2], 26, 197; Béchamp, *Ann. Chim. Phys.*, 1859, [3], 56, 306; [3], 57, 296.

chlorochromate,  $\text{Cr}_3\text{O}_6\text{Cl}_2$  (see p. 30), is known,<sup>1</sup> and two compounds,  $(\text{CrO}_2)_2\text{Cl}_6$  and  $\text{Cr}_6\text{O}_{13}\text{Cl}_4$ , obtained by the action of nitric oxide, or, in sunlight, of carbon monoxide upon chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , have been prepared.<sup>2</sup> The former,  $(\text{CrO}_2)_2\text{Cl}_6$ , which possesses chlorinating and oxidising properties, forms brown deliquescent crystals, and decomposes on heating to  $150^\circ\text{C}$ . into chromyl chloride, or, if heated rapidly, into chlorine, and  $\text{Cr}_3\text{O}_6\text{Cl}_2$ , which remains as a solid residue. Above  $180^\circ\text{C}$ . it yields oxygen and a brownish-black residue of  $\text{Cr}_6\text{O}_{13}\text{Cl}_4$ . The oxychloride,  $\text{Cr}_2\text{OCl}_4$ , is obtained by the action of hydrochloric acid on the hydroxide,  $\text{Cr}_2\text{O}(\text{OH})_4$ . Another, of the formula  $\text{CrOCl}_3$ , in which chromium appears to be pentavalent, forms double salts with the chlorides of the alkali metals and of certain organic bases. For instance,  $\text{CrOCl}_3 \cdot 2\text{KCl}$  is obtained as a red precipitate by treating with hydrogen chloride a mixture of a solution of potassium chloride and a concentrated solution of chromic acid already saturated with hydrogen chloride, and the mixture maintained at a low temperature.<sup>3</sup> A compound,  $\text{Cr}_2\text{O}_5\text{Cl}_2$ , is described as resulting from the heating of chromyl chloride with chromic anhydride in a sealed tube.<sup>4</sup>

**Chromyl Chloride,  $\text{CrO}_2\text{Cl}_2$** , sometimes termed *chlorochromic acid*, is readily prepared by distilling a mixture of fused potassium chromate or dichromate and sodium chloride with concentrated sulphuric acid :<sup>5</sup>



and, in order to remove free chlorine, repeatedly fractionating the distillate over mercury in a current of carbon dioxide. It is more expeditiously obtained, however, by dissolving chromic anhydride,  $\text{CrO}_3$ , in concentrated hydrochloric acid, and adding excess of concentrated sulphuric acid, when chromyl chloride is formed, which sinks to the bottom and may readily be separated. After aspirating dry air through the liquid in order to remove dissolved hydrochloric acid, it is subjected, as before, to fractional distillation.<sup>6</sup> Other methods of formation are : (a) by heating together<sup>7</sup> two equivalents of chromic chloride and three of chromic anhydride, or equal parts of the latter and ferric chloride ; (b) by passing hydrogen chloride over chromic anhydride ;<sup>8</sup> (c) by heating together phosphorus pentachloride and either chromic anhydride or potassium dichromate ;<sup>9</sup> (d) by the action of chlorine or hydrochloric acid upon the sesquioxide ;<sup>10</sup> (e) by heating together dry powdered chromic acid, acetyl chloride, and a little glacial acetic acid in carbon tetrachloride solution.<sup>11</sup> It is also produced by heating a chlorochromate with sulphuric acid, or by heating the oxychloride  $(\text{CrO}_2)_2\text{Cl}_6$  (q.v.).

<sup>1</sup> Thorpe, *J. Chem. Soc.*, 1870, 23, 31 ; *Jahresber.*, 1870, p. 330.

<sup>2</sup> Pascal, *Compt. rend.*, 1900, 148, 1403.

<sup>3</sup> Weinland and Friedrich, *Ber.*, 1905, 38, 3784 ; Weinland and Fiedorer, *ibid.*, 1906, 39, 4042 ; 1907, 40, 2090.

<sup>4</sup> Herfeldt, *J. prakt. Chem.*, 1894, 50, 93.

<sup>5</sup> Thomson, *Phil. Trans.*, 1827, 117, 169 ; Wöhler, *Pogg. Annalen*, 1834, 33, 343 ; Moles and Gómez, *Anal. Fis. Quim.*, 1912, 10, 43.

<sup>6</sup> Henry, *Ber.*, 1877, 10, 2041 ; Hounmann and Köchlin, *ibid.*, 1882, 15, 1116 ; Moissan, *Compt. rend.*, 1884, 98, 1582 ; Law and Perkin, *Trans. Chem. Soc.*, 1907, 97, 191.

<sup>7</sup> Geuther, *Annalen*, 1853, 106, 239 ; 1861, 118, 69.

<sup>8</sup> Moissan, *Ann. Chim. Phys.*, 1885, [9], 5, 568.

<sup>9</sup> Schiff, *Annalen*, 1858, 106, 116.

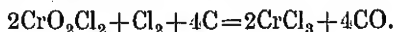
<sup>10</sup> Autenrieth, *Ber.*, 1902, 35, 2057.

<sup>11</sup> Fry, *J. Amer. Chem. Soc.*, 1911, 33, 697.

Chromyl chloride is a dark red, mobile liquid, of mean density 1.9587 at 0° C.<sup>1</sup> It boils at 116.68° C. under 760 mm. pressure, and the solid melts at  $-96.5 \pm 0.5^\circ$  C. It has been suggested for use as an ebulliscope solvent,<sup>2</sup> and gives a constant of 55 with chromic anhydride. Its yellowish-red vapour, which absorbs all the light from a luminous source except a narrow band in the red,<sup>3</sup> has a density<sup>4</sup> at temperatures up to 200° C. of 5.85 (air=1) corresponding to the formula  $\text{CrO}_2\text{Cl}_2$ .

Chromyl chloride fumes in air owing to the fact that it is decomposed by water into chromic and hydrochloric acids. The fumes when introduced into a Bunsen flame exhibit a characteristic spectrum.<sup>5</sup> When sufficiently purified by distillation, and free from access to moisture, chromyl chloride may be kept unchanged for a considerable time,<sup>6</sup> though on very long standing some dark coloured solid—probably a polymeride—is deposited.<sup>7</sup> This tendency to polymerise is also suggested by the results of cryoscopic molecular weight determinations in carbon tetrachloride, tin tetrabromide, or antimony pentachloride.

When heated in a sealed tube at 180° C. for three hours, chromyl chloride is converted to chromium chlorochromate (tri-chromyl chloride)<sup>8</sup> and chlorine, while by passing through a tube heated at 400° C., a grey or black deposit is obtained, consisting largely of the magnetic oxide,  $\text{Cr}_3\text{O}_8$ ;<sup>9</sup> at red heat the sesquioxide is formed. It readily parts with oxygen and chlorine, and is therefore an energetic oxidising and chlorinating agent, for example, towards sulphur, hydrogen sulphide, phosphorus (with explosion), hydrogen phosphide, phosphorus trichloride (see p. 91) and oxychloride, alcohol, turpentine, benzene and other hydrocarbons, fats, camphor, caoutchouc, and organic substances in general.<sup>10</sup> In dry ammonia it burns,<sup>11</sup> forming ammonium chloride and chromium dioxide (see p. 89). When ammonia gas is passed into a solution of chromyl chloride in acetic acid or chloroform, a slightly soluble brown substance, having the composition  $\text{Cr}_3\text{O}_8(\text{ONH}_4)_2$ , is formed.<sup>12</sup> A mixture of gaseous chromyl chloride and dry chlorine passed over carbon heated to redness yields chromic chloride in a well-crystallised condition. The course of the reaction appears to be :<sup>13</sup>



<sup>1</sup> Moles and Gómez, *Anal. Fis. Quim.*, 1912, 10, 43. For earlier values, see Thomson, *Pogg. Annalen*, 1834, 31, 607; Walter, *Ann. Chim. Phys.*, 1837, 66, 387; Thorpe, *Trans. Chem. Soc.*, 1880, 37, 327; Carstanjen, *J. prakt. Chem.*, 1897, [2], 2, 56.

<sup>2</sup> Beekmann, *Zeitsch. anorg. Chem.*, 1912, 77, 90.

<sup>3</sup> Stoney and Reynolds, *Phil. Mag.*, 1871, [4], 41, 291; *B.A. Reports*, 1878, ii., 434.

<sup>4</sup> Carstanjen, *loc. cit.*; Moles and Gómez, *Zeitsch. physikal. Chem.*, 1912, 80, 513; Dumas, *Ann. Chim. Phys.*, 1826, 31, 435; Walter, *loc. cit.*

<sup>5</sup> Gottschalk and Drechsel, *J. prakt. Chem.*, 1863, 89, 473.

<sup>6</sup> Etard, *Ann. Chim. Phys.*, 1881, [5], 22, 218; Carstanjen, *loc. cit.*; Law and Perkin, *Trans. Chem. Soc.*, 1907, 91, 191.

<sup>7</sup> Moles and Gómez, *Anal. Fis. Quim.*, 1914, 12, 142.

<sup>8</sup> Thorpe, *Trans. Chem. Soc.*, 1878, 8, 41; Schafarik, *Bull. Soc. chim.*, 1864, 1, 21.

<sup>9</sup> Soné and Ishiwara, *Sci. Rep. Tôhoku Imp. Univ.*, 1914, 3, 271. See also Wöhler, *Annalen*, 1859, 111, 117; *Pogg. Annalen*, 1834, 33, 331.

<sup>10</sup> Liebig, *Pogg. Annalen*, 1831, 21, 359; Schrötter, *Annalen*, 1841, 37, 148; Hointze, *J. prakt. Chem.*, 1871, [2], 4, 211; Carstanjen, *ibid.*, 1870, [2], 2, 51; *Ber.*, 1869, 2, 632; Etard, *Compt. rend.*, 1877, 84, 391; *Bull. Soc. chim.*, 1877, [2], 27, 249; Kemp, *J. Pharm.*, 1834, 20, 413; Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 449; Spence and Galletly, *J. Amer. Chem. Soc.*, 1911, 33, 190; Schiff, *Annalen*, 1857, 102, 111; Casselmann, *ibid.*, 1856, 98, 213; Weber, *Pogg. Annalen*, 1859, 107, 375; Cronander, *Ber.*, 1873, 6, 1466.

<sup>11</sup> Rideal, *Trans. Chem. Soc.*, 1880, 49, 367.

<sup>12</sup> Heintze, *loc. cit.*

<sup>13</sup> Mourelle and Banús, *Anal. Fis. Quim.*, 1910, 8, 355.

Chromyl chloride absorbs chlorine readily; it dissolves iodine,<sup>1</sup> forming a solution which on heating yields trichromyl chloride,  $\text{Cr}_3\text{O}_6\text{Cl}_2$  (see below), and iodine monochloride; with an aqueous solution of potassium chloride, potassium chlorochromate (see p. 68) is produced.<sup>2</sup>

Neither bromine nor iodine forms compounds analogous to chromyl chloride under any of the conditions given above (*cf.* p. 31), consequently the presence of a chromate in the aqueous solution of the distillate obtained by distilling a chloride, bromide, or iodide, or a mixture of these, with potassium dichromate and concentrated sulphuric acid, is sufficient evidence of the presence of a chloride in the mixture investigated (see p. 106).

**Trichromyl Chloride**,  $\text{Cr}_3\text{O}_6\text{Cl}_2$ , also known as *chromium chlorochromate*, is formed, together with chromyl chloride, when potassium chlorochromate,  $\text{Cl}.\text{CrO}_2.\text{OK}$ , is distilled with concentrated sulphuric acid;<sup>3</sup> by distilling a solution of iodine in chromyl chloride (see above); and by the action of chlorine upon chromium chromate (chromium dioxide). It is prepared by heating chromyl chloride in a closed tube for several hours at  $180^\circ\text{C}$ . as a black, amorphous, deliquescent powder, the aqueous solution of which evolves chlorine. It is readily reduced by hydrogen and is decomposed on heating in air. With hydrochloric acid, chlorine and chromic chloride are produced, while ammonia yields ammonium chloride and chromium chromate.<sup>4</sup>

**Chromium Chlorate**,  $\text{Cr}(\text{ClO}_3)_3$ , which is obtained by the double decomposition of barium chlorate and chrome alum, forms a violet solution which becomes green at  $65^\circ\text{C}$ . and decomposes on boiling, yielding chromium hydroxide and oxides of chlorine. The decomposition is facilitated by potassium ferrieyanide.<sup>5</sup> The salt is used in calico printing<sup>6</sup> and for increasing the permanence of aniline black.

**Chromium Perchlorate**.—By dissolving chromium hydroxide in perchloric acid, and subsequent cautious evaporation, short green deliquescent needles of chromium perchlorate, soluble in alcohol, are obtained.<sup>7</sup> Two bluish-green perchlorates, probably derivatives of the hex-aquo base,  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$  and  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3.3\text{H}_2\text{O}$ , have been described.<sup>8</sup>

#### CHROMIUM AND BROMINE.

**Chromous Bromide**,  $\text{CrBr}_2$ , is obtained by passing hydrogen bromide, or nitrogen saturated with bromine vapour, over strongly heated chromium, or by heating chromic bromide in hydrogen.<sup>9</sup> It is a white crystalline solid, which becomes yellowish on fusion and yields a green basic chromic bromide on exposure to air. It is soluble in water, forming a blue solution which can dissolve large quantities of violet chromic chloride, and which rapidly absorbs oxygen from the air. The solution may be prepared by heating a dilute solution of chromic acid with hydrobromic acid and reducing with zinc.

<sup>1</sup> MoIvor, *Chem. News*, 1873, 28, 138.

<sup>2</sup> Péligot, *Ann. Chim. Phys.*, 1833, 52, 267.

<sup>3</sup> Zettinow, *Pogg. Annalen*, 1871, 143, 328.

<sup>4</sup> Thorpe, *Trans. Chem. Soc.*, 1870, 8, 41.

<sup>5</sup> Prudhomme, *Chem. Zentr.*, 1890, i., 608; Saget, *ibid.*, 1902, i., 97.

<sup>6</sup> Despieres and others, *Dingl. poly. J.*, 1878, 228, 200.

<sup>7</sup> Goldblum and Terlikowski, *Bull. Soc. chim.*, 1912, [4], ii, 103.

<sup>8</sup> Weinland and Engraber, *Zeitsch. anorg. Chem.*, 1913, 84, 368.

<sup>9</sup> Wöhler and Bauck, *Annalen*, 1859, 111, 383; Moissan, *Compt. rend.*, 1881, 92, 1051; *Ann. Chim. Phys.*, 1882, [5], 25, 409.

**Chromic Bromide,  $\text{CrBr}_3$ ,** sublimes as dark green, lustrous hexagonal crystals, slightly dichroic,<sup>1</sup> when pellets of an intimate mixture of carbon and chromium sesquioxide are heated in dry bromine vapour, or when strongly heated chromium is acted upon by bromine vapour in an atmosphere of nitrogen.<sup>2</sup> When chromic bromide is heated in air, chromium sesquioxide is formed; it is easily reduced by hydrogen, and is attacked by fluorine at a red heat. The anhydrous salt is insoluble in water, but dissolves in the presence of a little chromous salt. A green solution is also obtained by dissolving chromic hydroxide in aqueous hydrobromic acid, or by digesting silver chromate in an alcoholic solution of hydrogen bromide. The hexahydrate,  $\text{CrBr}_3 \cdot 6\text{H}_2\text{O}$ , exists in two isomeric modifications,<sup>3</sup> as bluish-grey ("violet") and green crystals respectively, the former being stable in solution. The green variety, *dibromtetraquochromic bromide*  $[(\text{H}_2\text{O})_4\text{CrBr}_2]\text{Br} \cdot 2\text{H}_2\text{O}$ , is obtained as green deliquescent needles by evaporating a mixture of a saturated solution of chromic acid with excess of 50 per cent. hydrobromic acid. The crystals are soluble in water and alcohol, but insoluble in ether; in the solid phase they are stable, but in solution, especially on warming, the violet modification is rapidly<sup>4</sup> formed with evolution of heat. On boiling a concentrated solution of the green salt, and saturating with hydrogen bromide after cooling, the violet hydrate, *hexaquochromium bromide*  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$ , is deposited in fine hygroscopic crystals, very soluble in water, but insoluble in alcohol. The heat of transformation of the violet to the green variety is 2.15 Calories per gram-molecule.<sup>5</sup> An octahydrate,  $\text{CrBr}_3 \cdot 8\text{H}_2\text{O}$ , is described<sup>6</sup> in the form of violet cubic crystals, obtained by the interaction of potassium trichromate (see p. 62) and hydrobromic acid. The double salt,  $[(\text{H}_2\text{O})\text{CrBr}_2]\text{Rb}_2$ , is stated<sup>7</sup> to exist.

**Complex Halogen-halides.**—Two salts, *dichlorotetraquochromic bromide*  $[(\text{H}_2\text{O})_4\text{CrCl}_2]\text{Br}$  and *dibromtetraquochromic chloride*  $[(\text{H}_2\text{O})_4\text{CrBr}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ , have been described,<sup>8</sup> as also has the compound,  $\text{Cr}_2\text{F}_2\text{Cl}_4$ .<sup>9</sup>

There is some reason for the belief<sup>10</sup> that the interaction of chromic acid and acetyl bromide causes intermediate formation of unstable chromyl bromide,  $\text{CrO}_2\text{Br}_2$ .

**Chromium Bromate,  $\text{Cr}(\text{BrO}_3)_3$ ,** is said to have been obtained by evaporation of the filtrate from a mixture of chromic sulphate and barium bromate.<sup>11</sup>

#### CHROMIUM AND IODINE.

**Chromous Iodide,  $\text{CrI}_2$ ,** can be prepared<sup>12</sup> by the action of hydrogen iodide on chromium at a red heat, or by the reduction of chromic iodide by means of hydrogen. Reduction in solution produces

<sup>1</sup> Wöhler, *Annalen*, 1859, **111**, 382.

<sup>2</sup> Berthemot, *Ann. Chim. Phys.*, 1830, **44**, 383; Wöhler and Bauck, *loc. cit.*; Moissan, *loc. cit.*

<sup>3</sup> Recoura, *Compt. rend.*, 1890, **110**, 1029, 1193; Werner, *Annalen*, 1902, **322**, 290.

<sup>4</sup> Heydweiller, *Zeitsch. anorg. Chem.*, 1915, **91**, 66.

<sup>5</sup> Recoura, *loc. cit.*

<sup>6</sup> Varenne, *Compt. rend.*, 1881, **93**, 727.

<sup>7</sup> Werner, *loc. cit.*

<sup>8</sup> Bjerrum, *Ber.*, 1907, **40**, 2917.

<sup>9</sup> Recoura, *Compt. rend.*, 1913, **157**, 1525.

<sup>10</sup> Fry, *J. Amer. Chem. Soc.*, 1911, **33**, 697.

<sup>11</sup> Rammelsberg, *Pogg. Annalen*, 1842, **55**, 87.

<sup>12</sup> Moissan, *Compt. rend.*, 1881, **92**, 1051; *Ann. Chim. Phys.*, 1882, [5], **25**, 409.



a hydrate associated with a salt of zinc. Chromous iodide is a greyish-white powder, soluble in water; the solution absorbs oxygen, giving a green solution. Its general properties are similar to those of the other chromous halides.

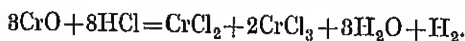
**Chromic Iodide,  $\text{CrI}_3$ .**—Moissan states that, by the action of iodine vapour in a current of nitrogen upon chromium at a red heat, reddish crystals of chromic iodide are obtained. An uncrystallisable solution is produced by digestion of silver chromate in alcoholic hydriodic acid.

**Chromium Iodate,  $\text{Cr}(\text{IO}_3)_3$ ,** is formed as a brown precipitate by the addition of sodium iodate to a solution of chromic chloride.<sup>1</sup>

#### CHROMIUM AND OXYGEN.

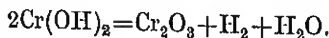
Four well-defined oxides of chromium are known :—chromous oxide,  $\text{CrO}$ ; chromic oxide,  $\text{Cr}_2\text{O}_3$ ; chromium dioxide,  $\text{CrO}_2$ ; and chromium trioxide,  $\text{CrO}_3$ . Chromous oxide, in which the metal is divalent, is basic in character and gives rise to the chromous series of salts; chromic oxide, containing trivalent chromium, has both basic and acidic properties, since, on the one hand, it gives rise to chromic salts, and on the other, it is soluble in alkalis with the formation of chromites; the dioxide,  $\text{CrO}_2$ , may be regarded as chromic chromate,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ ; chromium trioxide, which contains hexavalent chromium, possesses only acidic characters, combining with alkalis to form chromates. A number of other oxides, which may be regarded as compounds of the above, have also been described. The heptoxide,  $\text{Cr}_2\text{O}_7$ , regarded as the basis of some of the perchromates, has not been isolated.

**Chromous Oxide,  $\text{CrO}$ ,** is obtained<sup>2</sup> by the oxidation in air of chromium amalgam; or, preferably, by the action<sup>3</sup> of dilute nitric acid upon chromium amalgam. It is a black powder which inflames<sup>4</sup> when struck with a pestle, or when heated in the air, but not in a vacuum, and burns, forming the sesquioxide. It is insoluble in nitric acid and in dilute sulphuric acid, but in hydrochloric acid it dissolves, forming a blue solution and liberating hydrogen in accordance with the equation :



When heated to  $1000^\circ \text{C}$ . in a stream of carbon monoxide it is converted into a mixture of oxide and carbide, while hydrogen under the same conditions reduces it to the metal.<sup>5</sup>

When an air-free solution of caustic potash is added to a solution of chromous chloride in absence of air, a brownish-yellow precipitate of *chromous hydroxide*,  $\text{Cr}(\text{OH})_2$ , is obtained which may be dried over sulphuric acid. On heating in the presence of an inert gas this does not yield chromous oxide, since it decomposes<sup>6</sup> according to the equation :



**Chromo-chromic Oxides.**—Two hydrated oxides,  $\text{Cr}_3\text{O}_4 \cdot \text{H}_2\text{O}$  and

<sup>1</sup> Wulz, *Chem. News*, 1872, 26, 245; Rose, *Pogg. Annalen*, 1833, 27, 575; Giraud, *Phil. Mag.*, 1833, 12, 322.

<sup>2</sup> Férée, *Bull. Soc. chim.*, 1901, [3], 25, 619; Moberg, *J. prakt. Chem.*, 1848, 43, 119.

<sup>3</sup> Dieckmann and Hanf, *Zeitsch. anorg. Chem.*, 1914, 86, 301.

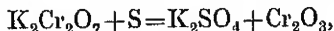
<sup>4</sup> Férée, *loc. cit.*

<sup>5</sup> Dieckmann and Hanf, *loc. cit.* Cf. Charpy, *Compt. rend.*, 1900, 148, 560.

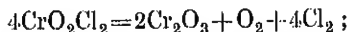
<sup>6</sup> Moberg, *J. prakt. Chem.*, 1848, 43, 119; Péligot, *Ann. Chim. Phys.*, 1844, [3], 12, 528. See also Manchot and Wilhelms, *Annalen*, 1902, 325, 125.

$2\text{Cr}_3\text{O}_4 \cdot 4\text{H}_2\text{O}$ , are said to exist, the former being described by Pélégot<sup>1</sup> as a product of the action of heat on chromous hydroxide, while the latter is obtained<sup>2</sup> as a yellowish-brown powder with vigorous reducing properties, stable in dry air, but decomposed on heating, by the decomposition of the double chromous potassium carbonate with boiling water in absence of air. The existence of an oxide, of composition  $2\text{CrO} \cdot \text{CrO}_3$  or  $8\text{CrO} \cdot \text{CrO}_3$  described by Bunsen,<sup>3</sup> has not been confirmed.<sup>4</sup>

**Chromic Oxide, Chromium Sesquioxide,  $\text{Cr}_2\text{O}_3$** , which occurs naturally in chrome ochre (see p. 8), exists in both amorphous and crystalline forms. The amorphous form may be obtained by calcination of a mixture of three parts of potassium chromate with two parts of sal-ammoniac;<sup>5</sup> by heating potassium dichromate with sulphur;<sup>6</sup>



or with starch,<sup>7</sup> and extraction of the residue with water; by gentle ignition of mercurous chromate or ammonium chromate; by heating finely divided chromium in oxygen; by ignition of chromic hydroxide,  $\text{Cr}(\text{OH})_3$ ; or by heating chromic chloride in air.<sup>8</sup> The substance can be obtained in the crystalline condition by passing chromyl chloride vapour through a red-hot porcelain tube<sup>9</sup> when the following reaction occurs:



by heating to bright redness a mixture of potassium chromate or dichromate with common salt;<sup>10</sup> by heating potassium chromate to redness in a current of chlorine, hydrogen chloride, or hydrogen;<sup>11</sup> by heating to redness potassium dichromate alone;<sup>12</sup> by fusion under suitable conditions of the amorphous oxide;<sup>13</sup> and by various other methods.<sup>14</sup>

Amorphous chromium sesquioxide is a green powder, the tint of which depends upon the method of preparation; the colour becomes brownish on heating. The crystalline oxide forms very dark green hard crystals belonging to the trigonal system (ditrigonal scalenohedral):<sup>15</sup>

$$a : c = 1 : 1.8770; \alpha = 85^\circ 22',$$

<sup>1</sup> Pélégot, *loc. cit.*

<sup>2</sup> Baugé, *Compt. rend.*, 1808, 127, 551.

<sup>3</sup> Bunsen, *Pogg. Annalen*, 1854, 91, 622.

<sup>4</sup> See Geuther, *Annalen*, 1861, 118, 66.

<sup>5</sup> Wöhler, *Pogg. Annalen*, 1827, 10, 46; de Luma, *Ann. Chim. Phys.*, 1863, [3], 68, 183; Böttger, *J. prakt. Chem.*, 1843, 30, 265; *Annalen*, 1843, 47, 339.

<sup>6</sup> Dieterich, *Zeitsch. Chem.*, 1860, p. 273; Lassaigne, *Ann. Chim. Phys.*, 1845, [3], 14, 299.

<sup>7</sup> Barian, *Annalen*, 1846, 60, 203.

<sup>8</sup> See also Berthier, *Ann. Chim. Phys.*, 1821, [2], 17, 56.

<sup>9</sup> Wöhler, *Pogg. Annalen*, 1834, 33, 341.

<sup>10</sup> Schiff, *Annalen*, 1858, 106, 114; Ditte, *Compt. rend.*, 1902, 134, 336.

<sup>11</sup> Frémy, *Annalen*, 1844, 49, 274; Müller, *Pogg. Annalen*, 1866, 127, 404; Otto, *Annalen*, 1867, 142, 102.

<sup>12</sup> Gentile, *J. prakt. Chem.*, 1860, 81, 418.

<sup>13</sup> Frémy, *Compt. rend.*, 1857, 44, 634; Sidot, *ibid.*, 1869, 69, 201; Ebelmen, *Ann. Chim. Phys.*, 1848, [3], 22, 211.

<sup>14</sup> See Klotzinsky, *Jahresber.*, 1866, p. 208; Evans, *Zeitsch. angew. Chem.*, 1891, 4, 18; Ebel, *Dingl. poly. J.*, 1876, 220, 64; Blake, *Annalen*, 1851, 78, 121; *Amer. J. Sci.*, 1850, [2], 10, 352.

<sup>15</sup> Strüver, *Mem. R. Accad. Lincei*, Rome, 1889, [4], 5, 519; *Zeitsch. Kryst. Min.*, 1891, 19, 207.

and isomorphous with aluminium and ferric oxides.<sup>1</sup> Its density is 5.04<sup>2</sup> and the mean values for its specific heat are as follows :<sup>3</sup>

Temperature, ° C.	Specific Heat.
-191 to -80.3	0.0711
-76.5 to 0	0.1474
+ 2.4 to +49.3	0.1805

It possesses magnetic properties.<sup>4</sup>

The crystal structure has been investigated by the Hull powder method of obtaining X-ray diffraction patterns.<sup>5</sup> The molecule is hexahedral, consisting of three atoms of oxygen at the corners of an equilateral triangle with two chromium atoms immediately above and below the centre of the triangle, three such molecules forming a unit prism.

Though difficult to fuse by ordinary methods, chromium sesquioxide melts readily in the electric furnace. The substance is undecomposed by heat,<sup>6</sup> and is not reduced by heating in hydrogen or carbon monoxide.<sup>7</sup> It is only reduced by carbon when an intimate mixture is very strongly heated; it is reduced by magnesium, aluminium, and the alkali metals at high temperatures.<sup>8</sup> On heating the unignited oxide at 440° C. in oxygen, Moissan<sup>9</sup> obtained the "dioxide," CrO<sub>2</sub>. The sesquioxide is readily attacked and oxidised by fused potassium nitrate, chlorate, hydrogen sulphate, or permanganate; by any suitable base in presence of oxygen; or by lead dioxide or manganese dioxide in presence of sulphuric acid.<sup>10</sup> Heated in dry air with potassium chloride, some chlorine is evolved;<sup>11</sup> if heated alone in a current of chlorine, chromic chloride is formed, while if hydrates are present, chromyl chloride is also formed. It also yields chromic chloride when mixed with carbon and heated in a current of chlorine, or by heating with phosphorus trichloride, or by interaction with sulphur chloride (see p. 25).<sup>12</sup>

<sup>1</sup> Rose, *Pogg. Annalen*, 1834, 33, 344.

<sup>2</sup> Clarke, *Constants of Nature*, pt. 1, Washington. See also Wöhler and Rose, *Pogg. Annalen*, 1834, 33, 341, 344; Ebelmen, *Ann. Chim. Phys.*, 1847, 22, 236; Frémy, *Annalen*, 1844, 49, 274; Schiff, *ibid.*, 1858, 106, 114; Schröder, *Pogg. Annalen*, 1859, 106, 226.

<sup>3</sup> Russell, *Physikal. Zeitsch.*, 1912, 13, 59. Kopp (*Annalen Supplement*, 1864, 3, 204) gave the value 0.177.

<sup>4</sup> Faraday, *Pogg. Annalen*, 1847, 70, 33; Nilson and Pettersson, *Ber.*, 1880, 13, 1450; Honda and Soné, *Sci. Rep. Tôhoku Imp. Univ.*, 1914, 3, 223; Wedekind and Horst, *Ber.*, 1915, 48, 105.

<sup>5</sup> Davey, *Phys. Review*, 1923, 21, 716.

<sup>6</sup> Elsner, *Jahresber.*, 1866, p. 35.

<sup>7</sup> Bell, *Chem. News*, 1871, 23, 258.

<sup>8</sup> Parkinson, *Trans. Chem. Soc.*, 1853, 5, 309; Gattermann, *Ber.*, 1880, 22, 107. See also p. 9.

<sup>9</sup> Moissan, *Ann. Chim. Phys.*, 1880, [5], 21, 199.

<sup>10</sup> Liebig and Wöhler, *Pogg. Annalen*, 1832, 24, 171; Böhlig, *Zeitsch. anal. Chem.*, 1890, 9, 357; Storer, *Jahresber.*, 1850, p. 680.

<sup>11</sup> Hargreaves and Robinson, *Ber.*, 1872, 5, 1064.

<sup>12</sup> Weber, *Pogg. Annalen*, 1861, 112, 619; *ibid.*, 1859, 107, 375; Moissan, *loc. cit.*; Maignon and Bourion, *Compt. rend.*, 1904, 138, 760. For other reactions, see Ashby, *Phil. Mag.*, 1853, [4], 6, 77; Martinon, *Bull. Soc. chim.*, 1880, [2], 45, 804.

Anhydrous chromic oxide, if it has not been strongly heated, though insoluble in water, is soluble in acids, with the formation of chromic salts; if heated to redness, a glow passes over the mass at  $500^{\circ}$  to  $610^{\circ}$  C.<sup>1</sup> and the substance is generally stated<sup>2</sup> to become, like the crystalline form, insoluble in water, alkalies, and acids.<sup>3</sup> It is, however, soluble in acids to a certain extent. For analytical purposes, the oxide, especially after strong ignition or when in the form of chromite, is best fused with a mixture of sodium carbonate (2 parts) and potassium nitrate (1 part) for ten minutes, the resulting mass extracted with water and the insoluble residue again fused with potassium pyrophosphate.<sup>4</sup>

**Chromic Hydroxide,  $\text{Cr}_2\text{O}_3 \cdot \text{Aq.}$** , is obtained by precipitation of a solution of a chromic salt by means of potassium hydroxide; if excess is used, the precipitate dissolves, forming a green solution from which the hydroxide is again precipitated on keeping or boiling.<sup>5</sup> Such precipitate retains alkali which cannot be removed by repeated washing with hot water; it is usual, therefore, to employ ammonium hydroxide as the precipitating agent. Even in this case, excess of ammonia dissolves chromic hydroxide, yielding a reddish-violet solution: methylamine behaves similarly, but di- and tri-methylamine at once precipitate chromic hydroxide completely. When freshly formed, the precipitate appears to be a well-defined chemical compound, the solubility product of which, according to Bjerrum,<sup>6</sup> is  $4.2 \times 10^{-16}$  at  $0^{\circ}$  C. and  $5.4 \times 10^{-16}$  at  $17^{\circ}$  C. in 0.0001 molar units. According to Weiser,<sup>7</sup> however, the precipitate obtained by the addition of alkali to solutions of chromic salts does not contain any definite hydrate. In the cold, the freshly formed precipitate readily dissolves in acids, but becomes insoluble on keeping or heating; between these two extremes of solubility an indefinite number of hydrous oxides exists. By precipitating at temperatures ranging from  $0^{\circ}$  C. to  $225^{\circ}$  C., products have been obtained varying in colour from greyish blue to bright green. Since most of the chromic salts exist in two distinct modifications (see p. 20), the violet and the green, it has long been assumed that there must be two isomeric chromic hydroxides corresponding to these two series of salts.<sup>8</sup> Such isomerides have not, however, been isolated. The properties of chromic hydroxide vary considerably with age, especially as regards solubility in acids and alkalies, and the "ageing" is accelerated if the precipitate is allowed to remain under alkaline solution; the rate appears to

<sup>1</sup> Mixtor, *Amer. J. Sci.*, 1915, [4], 39, 295.

<sup>2</sup> Compare Jovitschitsch, *Monatsh.*, 1909, 30, 47.

<sup>3</sup> Traube, *Annalen*, 1848, 66, 88; Le Chatelier, *Bull. Soc. chim.*, 1887, [2], 47, 300; Goro, *Phil. Mag.*, 1865, [4], 29, 541.

<sup>4</sup> Sabalitschka and Bull, *Zeitsch. anal. Chem.*, 1924, 64, 322.

<sup>5</sup> Losokann, *Ber.*, 1879, 12, 56; see also p. 36, and Castelaz and Leune, *Bull. Soc. chim.*, 1898, [2], 10, 170; Baubigny, *Compt. rend.*, 1884, 98, 100; Moinecke, *Annalen*, 1891, 261, 341; Friok, *Pogg. Annalen*, 1828, 13, 494; Becquerel, *Compt. rend.*, 1868, 67, 1083; Graham, *Annalen*, 1862, 121, 53; van Bemmelen, *Rec. Trav. chim.*, 1888, 7, 114; Fischer and Herz, *Zeitsch. anorg. Chem.*, 1902, 31, 352; Herz, *Chem. Zentr.*, 1904, ii, 178; Woudstra, *Chem. Weekblad*, 1909, 6, 375.

<sup>6</sup> Bjerrum, *Zeitsch. physikal. Chem.*, 1910, 73, 724.

<sup>7</sup> Weiser, *J. Physical Chem.*, 1922, 26, 401; 1920, 24, 277.

<sup>8</sup> Löwel, *J. Pharm. Chim.*, 1845, [3], 7, 321, 401, 424; Lefort, *Compt. rend.*, 1850, 30, 416; Frémy, *ibid.*, 1858, 47, 883; Recoura, *ibid.*, 1886, 102, 865; 1895, 120, 1335; *Ann. Chim. Phys.*, 1887, [6], 10, 52, 60; *Bull. Soc. chim.*, 1891, [3], 6, 909; Wyruboff, *ibid.*, 1902, [3], 27, 616, 719; *Ann. Chim. Phys.*, 1908, [8], 13, 523.

increase with hydroxyl-ion concentration and also with increase of temperature,<sup>1</sup> and the change in properties appears to be due to change in the size of the particles.

Chromium hydroxide is not precipitated by ammonia in presence of tartaric acid or glycerol,<sup>2</sup> probably owing to complex formation in the case of the former, but with glycerol a colloidal solution appears to be formed.

An alkaline solution of chromic hydroxide dissolves various metallic oxides.<sup>3</sup> If the hydroxide is precipitated in the presence of other salts, for example, of magnesium, calcium, zinc, or lead, the hydroxides of these metals are also carried down; it has been observed that magnesium hydroxide is thus adsorbed far more readily by violet than by green chromic hydroxide.<sup>4</sup>

Hydrated chromium sesquioxide is an amorphous, green, very hygroscopic powder, which on heating in the air first forms the "dioxide," and finally the green anhydrous sesquioxide.<sup>5</sup> Whereas the hepta- and tetra-hydrates,  $\text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  (the former being converted into the latter *in vacuo*), are soluble in dilute acids, the monohydrate,  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , is insoluble.<sup>6</sup>

*Colloidal Chromium Hydroxide.*—The hydrosol is obtained as a deep green solution by the peptisation of the hydroxide by means of chromic chloride,<sup>7</sup> or by a solution of copper oxide in ammonia. As already stated, the freshly precipitated hydroxide forms an apparently clear green solution with excess of an alkali hydroxide. That the chromic hydroxide is peptised and not dissolved is shown by the fact that it can be completely filtered out by means of a collodion filter,<sup>8</sup> leaving a colourless filtrate. The colloidal solution is stable while hot, but slowly yields a gel on keeping at ordinary temperatures.<sup>9</sup>

When potassium hydroxide is added to solutions containing ferric chloride and chromium sulphate in varying proportions, the iron is not

<sup>1</sup> Fricke and Windhausen, *Zeitsch. anorg. Chem.*, 1924, 132, 273; *Zeitsch. physikal. Chem.*, 1924, 113, 248; Fricke and Weyer, *Zeitsch. anorg. Chem.*, 1924, 136, 321; cf. Fricke, *Zeitsch. Elektrochem.*, 1920, 26, 129.

<sup>2</sup> Hakomori, *J. Chem. Soc. Japan*, 1922, 43, 629.

<sup>3</sup> Prudhomme, *Chem. Zentr.*, 1890, 1, 668; Church, *Quart. J. Sci.*, 1853, 6, 54; Chancel, *Compt. rend.*, 1850, 43, 927; Leykauf, *J. prakt. Chem.*, 1840, 19, 127; Malaguti, *Ann. Chim. Phys.*, 1830, [2], 61, 433; Leccoq de Boisbaudran, *Compt. rend.*, 1888, 107, 490.

<sup>4</sup> Pelouze, *Ann. Chim. Phys.*, 1851, [3], 33, 5; Chancel, *Compt. rend.*, 1850, 43, 927; Strömholm, *Arkiv. Kem. Min. Geol.*, 1900, 2, No. 9, 1.

<sup>5</sup> Krüger, *Pogg. Annalen*, 1844, 61, 218, 407; *Annalen*, 1844, 52, 249; Slowort, *Zeitsch. gesamm. Naturwiss.*, 1861, 18, 244.

<sup>6</sup> Schrötter, *Pogg. Annalen*, 1841, 53, 513; Schaffner, *Annalen*, 1844, 51, 169; Prudhomme, *Chem. Zentr.*, 1890, 1, 609; Berzoli, *Pogg. Annalen*, 1838, 45, 183; 1851, 83, 143; Hortwig, *ibid.*, 1842, 56, 95; Löwel, *Jahresber.*, 1855, p. 376; Etard, *Compt. rend.*, 1876, 80, 1306; 1877, 84, 1089; Siewert, *Annalen*, 1863, 126, 94; Doyer van Cleef, *J. prakt. Chem.*, 1881, [2], 23, 58; Ber., 1881, 14, 250; Hartley, *Proc. Roy. Soc.*, 1875, 33, 372; *Chem. News*, 1892, 65, 15; Péligot, *Ann. Chim. Phys.*, 1845, [3], 14, 230; Herz, *Zeitsch. anorg. Chem.*, 1901, 28, 342; Berthelot, *Compt. rend.*, 1883, 96, 536; Thomsen, *Thermochemische Untersuchungen*, 1882, 1, 366; Petterson, *Ber.*, 1888, 21, 3257; Wyruboff, *Ann. Chim. Phys.*, 1908, [3], 13, 523; Ordway, *Amer. J. Sci.*, 1858, [2], 26, 107; Vincent, *Phil. Mag.*, 1857, [4], 13, 191.

<sup>7</sup> Graham, *Annalen*, 1862, 124, 168. See also Wintgen and Löwenthal, *Zeitsch. physikal. Chem.*, 1924, 109, 378.

<sup>8</sup> Fischer and Herz, *Zeitsch. anorg. Chem.*, 1902, 31, 352; Fischer, *ibid.*, 1904, 40, 39; Nagel, *J. Physical Chem.*, 1915, 19, 331, 569.

<sup>9</sup> Neidlo and Barab, *J. Amer. Chem. Soc.*, 1916, 38, 1961; 1917, 39, 71.

# LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

ABBREVIATED TITLE.	JOURNAL.
<i>Afhandl. Fys. Kem.</i> . . . .	Afhandlingar i Fysik, Kemi och Mineralogi.
<i>Amer. Chem. J.</i> . . . .	American Chemical Journal.
<i>Amer. J. Sci.</i> . . . .	American Journal of Science.
<i>Anal. Fis. Quim.</i> . . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . . .	The Analyst.
<i>Annalen</i> . . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim.</i> . . . .	Annales de Chimie (1719-1815, and 1914 +).
<i>Ann. Chim. anal.</i> . . . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
<i>Ann. Chim. Phys.</i> . . . .	Annales de Chimie et de Physique (Paris) (1816-1913).
<i>Ann. Mines</i> . . . .	Annales des Mines.
<i>Ann. Pharm.</i> . . . .	Annalen der Pharmacie (1832-1839).
<i>Ann. Phys. Chem.</i> . . . .	Annalen der Physik und Chemie (1819-1899).
<i>Ann. Physik</i> . . . .	Annalen der Physik (1799-1818, and 1900 +).
<i>Ann. Physik, Beibl.</i> . . . .	Annalen der Physik, Beiblätter.
<i>Ann. Sci. Univ. Jassy</i> . . . .	Annales scientifiques de l'Université de Jassy.
<i>Arbeiten Kaiserl. Gesundheitsamte</i> . . . .	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
<i>Arch. exp. Pathol. Pharmac.</i> . . . .	Archiv für experimentelle Pathologie und Pharmacologie.
<i>Arch. Pharm.</i> . . . .	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i> . . . .	Archives des Sciences physiques et naturelles, Genève.
<i>Atti Acc. Torino</i> . . . .	Atti della Reale Accademia dello Scienza di Torino.
<i>Atti R. Accad. Lincei</i> . . . .	Atti della Reale Accademia Lincei.
<i>B.A. Reports</i> . . . .	British Association Reports.
<i>Ber.</i> . . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Akad. Ber.</i> . . . .	Soo <i>Sitzungsber. K. Akad. Wiss. Berlin</i>
<i>Ber. Deut. physikal. Ges.</i> . . . .	Berichte der Deutschen physikalischen Gesellschaft.
<i>Bot. Zeit.</i> . . . .	Botanische Zeitung.
<i>Bull. Acad. Sci. Cracov</i> . . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. roy. Belg.</i> . . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. de Belg.</i> . . . .	Bulletin de la Société chimique Belgique.
<i>Bull. Soc. chim.</i> . . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. franc. Min.</i> . . . .	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. min. de France</i> . . . .	Bulletin de la Société minéralogique de France.
<i>Bull. U.S. Geol. Survey</i> . . . .	Bulletins of the United States Geological Survey.
<i>Centr. Min.</i> . . . .	Centralblatt für Mineralogie.
<i>Chem. Ind.</i> . . . .	Die Chemische Industrie.
<i>Chem. News</i> . . . .	Chemical News.
<i>Chem. Weekblad.</i> . . . .	Chemisch Weekblad.
<i>Chem. Zentr.</i> . . . .	Chemisches Zentralblatt.
<i>Chem. Zeit.</i> . . . .	Chemiker Zeitung (Cöthen).
<i>Compt. rend.</i> . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
<i>Crell's Annalen</i> . . . .	Chemische Annalen für die Freunde der Naturlehre, von L. Crell.
<i>Dingl. poly. J.</i> . . . .	Dingler's polytechnisches Journal.
<i>Drude's Annalen</i> . . . .	Annalen der Physik (1900-1906).
<i>Electroch. Met. Ind.</i> . . . .	Electrochemical and Metallurgical Industry.

**Cadmium Chromite**,  $\text{CdO} \cdot \text{Cr}_2\text{O}_3$ , is prepared by heating the chloride with potassium dichromate.<sup>1</sup> It yields green, hard crystals, of density 5.79 at 17° C.

**Calcium Chromite**,  $\text{CaO} \cdot \text{Cr}_2\text{O}_3$ , is an olive-green crystalline powder of density 4.8 at 18° C. and hardness 6. It is produced by heating together calcium chloride and potassium dichromate, and subsequent extraction with concentrated hydrochloric acid.<sup>2</sup> A compound,  $2\text{CaO} \cdot \text{Cr}_2\text{O}_3$ , is obtained<sup>3</sup> by the interaction of ammonia and aqueous chrome alum and calcium chloride, while by direct combination of the oxides in the electric furnace, transparent green crystals of composition  $4\text{CaO} \cdot \text{Cr}_2\text{O}_3$  are formed.<sup>4</sup>

**Cobalt Chromite**,  $\text{CoO} \cdot \text{Cr}_2\text{O}_3$ , is obtained by the addition of sodium carbonate to a mixed solution of chrome alum and cobalt chloride, and igniting the precipitate.<sup>5</sup>

By fusion of the mixed oxides it is obtained in the form of green octahedral crystals.<sup>6</sup>

**Cupric Chromite**,  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ , is a black crystalline powder.<sup>2</sup>

**Cuprous Chromite**,  $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ , yields steel-blue crystals, density 5.24.<sup>7</sup>

**Ferrous Chromite**,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ , occurs in nature as chrome iron ore (see p. 7). It has been obtained<sup>8</sup> in the form of octahedra, of density 4.97 and specific heat 0.159.

**Lead Chromite**,  $\text{PbO} \cdot \text{Cr}_2\text{O}_3$ , has been prepared.<sup>10</sup>

**Lithium Chromite**,  $\text{Li}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ , is produced by fusing lithium chromate with kaolin.<sup>11</sup> Brown octahedra.

**Magnesium Chromite**,  $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ , has been obtained by fusion of the mixed oxides. It yields green octahedra harder than quartz and of density 4.415 at 16° C. and 4.6 at 20° C.<sup>12</sup> Several other compounds of magnesium and chromic oxides are known<sup>13</sup> which may be represented by the formulæ:  $\text{MgO} \cdot 2\text{Cr}_2\text{O}_3$ ;  $2\text{MgO} \cdot \text{Cr}_2\text{O}_3$ ;  $3\text{MgO} \cdot 2\text{Cr}_2\text{O}_3$ ;  $5\text{MgO} \cdot 4\text{Cr}_2\text{O}_3$ .

**Manganese Chromite**,  $\text{MnO} \cdot \text{Cr}_2\text{O}_3$ , is a grey or black crystalline powder<sup>14</sup> of density 4.97.

**Nickel Chromite**,  $\text{NiO} \cdot \text{Cr}_2\text{O}_3$ , is prepared in an analogous manner to the cobalt salt (see also p. 8).

**Tungsten Chromite**,  $5\text{WO}_3 \cdot \text{Cr}_2\text{O}_3$ , has been prepared.<sup>15</sup>

<sup>1</sup> Viard, *Compt. rend.*, 1889, 109, 142; 1891, 112, 1003.

<sup>2</sup> Gerber, *Bull. Soc. chim.*, 1877, [2], 27, 436.

<sup>3</sup> Pelouze, *Ann. Chim. Phys.*, 1851, [3], 33, 5.

<sup>4</sup> Dufau, *ibid.*, 1897, [7], 12, 257; Moissan, *Bull. Soc. chim.*, 1902, 3, 27, 664.

<sup>5</sup> Elliott, *Magnetic Combinations* (Göttingen, 1862).

<sup>6</sup> Hedvall, *Zeitsch. anorg. Chem.*, 1915, 93, 313.

<sup>7</sup> Persoz, *Compt. rend.*, 1891, 53, 69; L. and P. Wöhler, *Zeitsch. physikal. Chem.*, 1908, 62, 440.

<sup>8</sup> Ebelmen, *Ann. Chim. Phys.*, 1851, [3], 33, 44; Gerber, *loc. cit.*; Mounier, *Compt. rend.*, 1888, 107, 1153.

<sup>9</sup> Kopp, *Annalen Supplement*, 1864, 3, 204.

<sup>10</sup> Chancel, *Compt. rend.*, 1856, 43, 927.

<sup>11</sup> Weyborg, *Centr. Min. Geol.*, 1906, p. 645; *Chem. Zentr.*, 1906, ii., 1659.

<sup>12</sup> Ebelmen, *loc. cit.*; Dufau, *loc. cit.* See also Schweitzer, *J. prakt. Chem.*, 1846, [1], 39.

<sup>13</sup> Gerber, *loc. cit.*; Persoz, *loc. cit.*

<sup>14</sup> Nichols, *Amer. J. Sci.*, 1869, [2], 47, 16; Krepis, *Dissertation*, Berlin, 1893; Dufau, *Compt. rend.*, 1895, 121, 680; 122, 1125; 1896, 123, 880; *Ann. Chim. Phys.*, 1897, [7], 12, 257; Viard, *Bull. Soc. chim.*, 1889, [3], 2, 331; 1891, [3], 5, 933.

<sup>15</sup> Ebelmen, *loc. cit.*; Gerber, *loc. cit.*

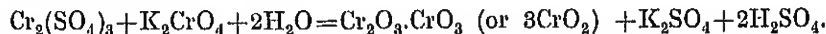
<sup>16</sup> Smith, *J. Amer. Chem. Soc.*, 1893, 15, 151.

**Zinc Chromite,  $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$ ,** may be obtained in the same manner as the corresponding calcium salt.<sup>1</sup> It yields dark green octahedral crystals of density 5.29 at 13° C. Two other zinc compounds are known,<sup>2</sup> namely:  $3\text{ZnO} \cdot 2\text{Cr}_2\text{O}_3$ ;  $6\text{ZnO} \cdot 5\text{Cr}_2\text{O}_3$ .

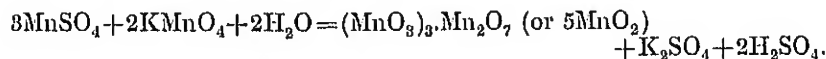
The chromites of the alkali metals and of ammonium are presumably formed to some extent in solution, when chromic hydroxide dissolves in excess of the alkali hydroxide;<sup>3</sup> but it has been shown that these solutions are in large degree merely colloidal solutions of the hydroxide (see p. 36). By shaking chromic hydroxide, dried over sulphuric acid, with solutions of sodium hydroxide of different concentrations, Müller<sup>4</sup> found that the amount of hydroxide dissolved depended on the time of agitation, rising to a maximum and then falling to an almost constant value. The solutions obtained were not colloidal. Fricke and Windhausen<sup>5</sup> have prepared similar solutions, and by allowing solutions of potassium chromite to stand for some time, obtained needle-shaped crystals of composition  $\text{Cr}_2\text{O}_3 \cdot 3\text{K}_2\text{O} \cdot 8\text{H}_2\text{O}$ .

The gradual separation of chromium hydroxide from clear chromite solutions is due to the "ageing" of chromium hydroxide already present in solution in the colloidal state.

**Chromium Dioxide,  $\text{CrO}_2$ ,** or chromic chromate,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , may be obtained<sup>6</sup> by heating the sesquioxide in air or oxygen;<sup>7</sup> or by interaction of chromic hydroxide and chromic acid, or of a chromic salt and a chromate.<sup>8</sup> Thus:



This reaction may be compared with the following:



The dioxide is also formed by suitable reduction of chromates, for example, by means of sodium hyposulphite, alcohol, nitric oxide, or a mixture of nitric and oxalic acids;<sup>9</sup> or by interaction of chromic chloride and bleaching powder.<sup>10</sup>

When prepared by the first method, the product is a light, hygroscopic, black powder, which at a red heat evolves oxygen and leaves a

<sup>1</sup> Viard, *loc. cit.*

<sup>2</sup> Gerber, *loc. cit.*; Chancel, *loc. cit.*; Viard, *Compt. rend.*, 1880, 109, 142; Ebelmon, *loc. cit.*

<sup>3</sup> Wood and Black, *Trans. Chem. Soc.*, 1910, 109, 104. See also Bourion and Sénéchal, *Compt. rend.*, 1910, 168, 59, 89; Jovitschitsch, *Helv. Chim. Acta*, 1920, 3, 46.

<sup>4</sup> Müller, *Zeitsch. angew. Chem.*, 1922, 35, 557.

<sup>5</sup> Fricke and Windhausen, *Zeitsch. anorg. Chem.*, 1924, 132, 273.

<sup>6</sup> A list of methods for the preparation of chromium dioxide is given by Ridley, *Chem. News*, 1924, 129, 35.

<sup>7</sup> Krüger, *Pogg. Annalen*, 1844, 61, 219; Moissan, *Ann. Chim. Phys.*, 1880, [5], 21, 199; Jovitschitsch, *loc. cit.*, 40.

<sup>8</sup> Maus, *Pogg. Annalen*, 1827, 9, 127; Beusoh, *ibid.*, 1842, 55, 98.

<sup>9</sup> Schweitzer, *J. prakt. Chem.*, 1846, 39, 269; Grouvello, *Ann. Chim. Phys.*, 1821, 17, 349; Elliot and Storer, *Jahresber.*, 1861, p. 251; Kopp, *Chem. News*, 1865, 11, 16; Popp, *Annalen*, 1870, 156, 90; Schwan, *Dingt. poly. J.*, 1871, 199, 130; Vogel, *J. prakt. Chem.*, 1859, 77, 482; Schiff, *Annalen*, 1861, 120, 207; 1874, 171, 110; Hintz, *ibid.*, 1873, 169, 367.

<sup>10</sup> Schiff, *loc. cit.* See also Traube, *Annalen*, 1848, 66, 106; Rammelsberg, *ibid.*, 1846, 60, 203; Braun, *J. prakt. Chem.*, 1863, 90, 356; Oppenheim, *Bull. Soc. chim.*, 1880, [3], 1, 165.



residue of the sesquioxide. It is only slightly attacked by hydrochloric or hydriodic acids, and possesses the properties of a dioxide,  $O=Cr=O$ , rather than those of a chromate.<sup>1</sup> Prepared by wet methods, it is a brown powder from which soluble  $Cr_2O_3$  can be removed by repeated washing with water, leaving a residue of insoluble  $Cr_2O_3$ , and which dries at  $250^\circ C.$  to a black hygroscopic powder. The latter, when heated with hydrochloric acid or in a current of hydrogen chloride, evolves chlorine.<sup>2</sup>

When an aqueous solution of chromic nitrate is treated with ammonia, a dark brown, almost black precipitate is produced,<sup>3</sup> analyses of which point to the formula  $Cr_2(OH)_8 \cdot H_2O$ , or  $CrO_3 \cdot Cr_2O_3 \cdot 7H_2O$ . Its behaviour on drying is more readily explained by the first formula, since it loses  $1H_2O$  over sulphuric acid,  $2H_2O$  when heated at  $105^\circ C.$ , and  $6H_2O$  at  $205^\circ C.$ ; however, Jovitschitsch favours the second formula as more nearly representing its chromium content. It is an unstable body and loses chromium trioxide on repeated washing with warm water. Pure chromium hydroxide free from alkali may be obtained from it by boiling its solution in concentrated hydrochloric acid with alcohol, until reduction is complete, and then adding ammonia in excess. Anhydrous chromium chromate cannot be obtained from it by heating, since it decomposes before the last molecule of water is removed.

The readiness with which chromium chromate is converted by ammonia, alkali carbonate, or hydroxide, or by boiling water, into chromium hydroxide and chromate is considered to be evidence of its salt-like constitution.

**Other Oxides.**— $Cr_5O_9$ , or  $2Cr_2O_3 \cdot CrO_3$ , is a violet, magnetic, insoluble compound, obtained by passing the vapour of chromyl chloride through a hot tube,<sup>4</sup> whilst the hydrate,  $Cr_5O_9 \cdot 9H_2O$ , is a voluminous, brownish, hygroscopic powder, soluble in dilute acids.<sup>5</sup>

The following have also been described, though the evidence with regard to their existence as definite compounds is more or less inconclusive:  $Cr_2O_4 \cdot 3H_2O$ ; <sup>6</sup>  $Cr_2O_3 \cdot 2CrO_3$ ; <sup>7</sup>  $Cr_2O_3 \cdot 3CrO_3$ ; <sup>8</sup>  $Cr_2O_3 \cdot 4CrO_3$ ; <sup>9</sup>  $Cr_6O_{15} \cdot 12H_2O$ ; <sup>10</sup> and  $8Cr_2O_3 \cdot 2CrO_3 \cdot 9H_2O$ .<sup>11</sup>

**Chromium Trioxide, Chromic Anhydride,  $CrO_3$ ,** was first obtained by Unverdorben by the interaction of chromyl fluoride and water.<sup>12</sup> It is usually prepared by the action of concentrated sulphuric acid on solutions of a chromate, usually of potassium dichromate.<sup>13</sup> Zettnow

<sup>1</sup> Hintz, *Annalen*, 1873, 169, 307; Manchot and Kraus, *Ber.*, 1900, 39, 3512.

<sup>2</sup> Moissan, *Ann. Chim. Phys.*, 1880, [5], 21, 243. For other reactions see Martinon, *Bull. Soc. chim.*, 1880, [2], 45, 804; Hintz, *loc. cit.*

<sup>3</sup> Jovitschitsch, *Helv. Chim. Acta*, 1920, 3, 40.

<sup>4</sup> Wöhler, *Annalen*, 1859, 111, 117; Geuther, *ibid.*, 1861, 118, 62; Bernoulli, *Chem. Zentr.*, 1904, ii, 1371; Soné and Ishiware, *Sci. Rep. Tôhoku Imp. Univ.*, 1914, 3, 271; Wedekind and Horst, *Ber.*, 1915, 48, 105.

<sup>5</sup> Popp, *Annalen*, 1870, 156, 90.

<sup>6</sup> Godefroy, *Bull. Soc. chim.*, 1883, [2], 40, 168.

<sup>7</sup> Shukoff, *Compt. rend.*, 1908, 146, 1396; Wedekind and Horst, *loc. cit.*

<sup>8</sup> Traube, *Annalen*, 1848, 66, 108; Hintz, *ibid.*, 1873, 169, 397.

<sup>9</sup> Maus, *loc. cit.*; Löwel, *J. Pharm. Chim.*, 1845, [3], 7, 321, 401, 424; Elliot and Storer, *Jahresber.*, 1861, p. 251; Honda and Soné, *Sci. Rep. Tôhoku Imp. Univ.*, 1914, 3, 223.

<sup>10</sup> Braun, *J. prakt. Chem.*, 1863, 90, 356.

<sup>11</sup> Rammelsberg, *Pogg. Annalen*, 1846, 68, 274; Traube, *loc. cit.*

<sup>12</sup> Unverdorben, *Trommsd. N.J. Pharm.*, 1824, 9, 26.

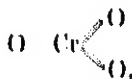
<sup>13</sup> Fritzsche, *Bull. Acad. Sci. Petrograd*, 1839, 131; Warrington, *J. prakt. Chem.*, 1842, 27, 262; Bolley, *Annalen*, 1845, 56, 113; Traube, *ibid.*, 1848, 66, 105; Bunson, *ibid.*, 1868, 148, 200; Zettnow, *Pogg. Annalen*, 1871, 143, 408; Niernus, *Chem. Zentr.*, 1873, p. 737.

recommends that 300 grams of potassium dichromate be warmed until dissolved with 500 c.c. of water after the addition of 420 c.c. of concentrated sulphuric acid; after standing for ten to twelve hours, the liquid is poured away from the potassium hydrogen sulphate crystals that have separated, heated to 80° to 90° C., and 150 c.c. of concentrated sulphuric acid added, then water, a few drops at a time, until the chromium trioxide crystals which separate at first are just redissolved. Crystals are allowed to deposit during twelve hours, and subsequently, after concentration, they are collected upon a platinum, asbestos, or pumice-stone filter, and washed with pure nitric acid of density 1.40. The crystals are then mixed with a little concentrated nitric acid, and dried upon a porous plate, the process being repeated until the product is quite free from potassium sulphate and sulphuric acid. The potassium sulphate may also be removed as potassium alum by addition of aluminium sulphate, and the sulphuric acid separated by fusion.<sup>1</sup> The crystals are freed from nitric acid by warming, preferably in a current of dry air in a tube at 60° to 80° C. Other methods of formation are by the action of concentrated sulphuric acid upon lead chromate;<sup>2</sup> from barium and strontium chromates by the action of sulphuric acid or nitric acid;<sup>3</sup> by the action of chlorine, or of hydrochloric acid upon silver chromate.<sup>4</sup> Commercial "pure chromic acid" has been found to contain a certain amount of sandy material; it can be purified sufficiently highly even for atomic weight determinations by repeated recrystallisation, after filtration, from distilled water.<sup>5</sup>

Chromium trioxide forms lustrous red needles, crystallising in the rhombic system (bipyramidal):

$$a : b : c = 0.002 : 1 : 0.028,^6$$

and having<sup>7</sup> a mean density of 2.74. It melts at 136° C. with slight decomposition,<sup>8</sup> the molten mass having a density of 2.8.<sup>9</sup> It is considered<sup>10</sup> to contain hexavalent chromium, being represented by the constitutional formula:



<sup>1</sup> Fitz-Gerald and Molloy, *Ber.*, 1876, 8, 177; Schmarzik, *Wied. Annalen*, 1892, 47, 264; Moissan, *Ann. Chim. Phys.*, 1886, [4], 5, 408.

<sup>2</sup> Schrötter, *Annalen*, 1843, 48, 226.

<sup>3</sup> Kuhlmann, *Ann. Chim. Phys.*, 1858, [3], 54, 400; Rowell, *Ber.*, 1886, 18, 677; Siewert, *Jahresber.*, 1892, p. 140; Davillier, *Compt. rend.*, 1872, 75, 711.

<sup>4</sup> Krutwig, *Ber.*, 1881, 14, 300; Thomson, *Pogg. Annalen*, 1870, 140, 613. There are several other methods. See Maillart, *Compt. rend.*, 1892, 94, 803; Mann, *Pogg. Annalen*, 1827, 9, 127; Prudhomme and Blaser, *Bull. Soc. chim.*, 1882, [2], 37, 104; Möller and Soller, *Zeitsch. Elektrochem.*, 1905, 11, 803; Aukemy and Rényi, *ibid.*, 1913, 19, 344; Piccard, *Ber.*, 1913, 46, 2477.

<sup>5</sup> Baxter, Mueller, and Hines, *J. Amer. Chem. Soc.*, 1909, 31, 629.

<sup>6</sup> Nordenskjöld, *Pogg. Annalen*, 1891, 114, 612.

<sup>7</sup> Clarke, *Constants of Nature*, pt. 1, Washington. See Zettnow, *Pogg. Annalen*, 1871, 143, 474.

<sup>8</sup> Gieschuff, *Zeitsch. anorg. Chem.*, 1908, 58, 102. See also Zettnow, *loc. cit.*; Traube, *Annalen*, 1848, 66, 105; Moissan, *Ann. Chim. Phys.*, 1883, [4], 5, 408.

<sup>9</sup> Zettnow, *loc. cit.*; Schmarzik, *J. prakt. Chem.*, 1893, 99, 16.

<sup>10</sup> Luther and Rutter, *Zeitsch. anorg. Chem.*, 1907, 54, 1; cf. Marchot and Kraus, *Ber.*, 1906, 39, 1352.

The anhydrous oxide is very soluble in water: the solubility in grams of solute per 100 grams of solution is as follows: <sup>1</sup>

Temperature, ° C.	Grams CrO <sub>3</sub> per 100 Grams Solution. <sup>1</sup>
0	61.2
20	62.5
40	63.5
60	64.65
80	65.9
100	67.4
120	69.5

A saturated solution at 22° C., containing 62.23 per cent. of chromium trioxide, has a density <sup>2</sup> of 1.7028. It is soluble in dilute alcohol, with slight decomposition in light or by heat, but is immediately decomposed by pure alcohol.<sup>3</sup> Several esters of chromic acid have been described.<sup>4</sup>

Chromium trioxide decomposes at 330° C. with deflagration, evolving oxygen.<sup>5</sup> Concentrated sulphuric acid dissolves it in the cold, probably with formation of compounds.<sup>6</sup> A powerful oxidising agent, it is very easily reduced by hydrogen, hydrochloric, hydrobromic, and hydriodic acids, phosphorus, hydrogen sulphide, hydrazine, etc., and by electrolysis.<sup>7</sup> Reduction is considered <sup>8</sup> to take place in three

<sup>1</sup> Interpolated from data given by Kromann, *Sitzungsber. K. Akad. Wiss. Wien*, 1911, 120, iii, 330; Koppel and Blumenthal, *Zeitsch. anorg. Chem.*, 1900, 53, 202; Mylius and Funk, *Wiss. Abhandl. Phys.-Tech. Reich.*, 1900, 3, 451.

<sup>2</sup> Zettnow, *Pogg. Annalen*, 1871, 143, 474. See also Morges, *Compt. rend.*, 1878, 86, 1443; Sabatier, *ibid.*, 1880, 103, 138, 207. For other thermal, electrical, etc., investigations, see Thomson, *Thermochemische Untersuchungen*, 1, 255; Bertholot, *Ann. Chim. Phys.*, 1884, [6], 1, 95; Sottogast, *Wied. Annalen*, 1879, 7, 242; Marignac, *Ann. Chim. Phys.*, 1876, [5], 8, 410; Ostwald, *Zeitsch. physikal. Chem.*, 1888, 2, 78; Field, *Chem. News*, 1892, 65, 162; Bleekrode, *Wied. Annalen*, 1878, 3, 162; Hittdorf, *ibid.*, 1878, 4, 374; Molati and Mascetti, *Gazzetta*, 1900, 30, 535; Morges, *Compt. rend.*, 1878, 87, 15; Riesenfeld and Wohlers, *Chem. Zentr.*, 1907, i, 219; Mixtor, *Amer. J. Sci.*, 1908, [4], 26, 125; Wedokind and Horst, *Ber.*, 1915, 48, 105.

<sup>3</sup> Traubo, *Millon and Reisel's Ann.*, 1849, p. 148.

<sup>4</sup> Jaques, *Chem. News*, 1907, 96, 77; Wionhaus, *Ber.*, 1914, 47, 322.

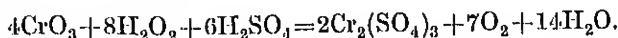
<sup>5</sup> Shukoff, *Compt. rend.*, 1908, 146, 1306.

<sup>6</sup> Bolley, *Annalen*, 1845, 56, 113; Schrötter, *ibid.*, 1843, 48, 225; Gawalowsky, *Zeitsch. anal. Chem.*, 1878, 17, 170.

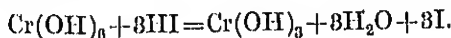
<sup>7</sup> Ludwig, *Annalen*, 1872, 162, 47; Road, *Chem. News*, 1907, 95, 169; Louis Henry, *Bull. Acad. roy. Belg.*, 1860, [2], 21, 230; Oppenheim, *Bull. Soc. chim.*, 1864, [2], 1, 165; Harten, *Annalen*, 1841, 37, 350; Seubert and Carstens, *Zeitsch. anorg. Chem.*, 1908, 56, 357; Favro, *Compt. rend.*, 1871, 73, 890, 936; Gauthier, *Annalen*, 1850, 99, 314; Buff, *ibid.*, 1859, 110, 257; de Lury, *J. Physical Chem.*, 1907, 11, 54. Also by iodine, *Waltz, Chem. News*, 1872, 26, 245; by sulphurous acid, Traubo, *Annalen*, 1848, 66, 103; by nitric oxide, Reinsch, *J. prakt. Chem.*, 1843, 28, 391; Wöhler, *Annalen*, 1840, 34, 236; by sulphur, Moissan, *Ann. Chim. Phys.*, 1885, [6], 5, 568; by arsenious oxide, de Lury, *J. Physical Chem.*, 1907, 11, 47; by ammonia, by cyanogen bromide, Guareschi, *Atti R. Accad. Sci. Torino*, 1914, 49, 15; by the alkali metals, Moissan, *Compt. rend.*, 1884, 98, 1581; *Ann. Chim. Phys.*, 1885, [6], 5, 468; by phosphorus pentachloride, Schiff, *Annalen*, 1858, 106, 116; by chromic chloride, Gauthier, *ibid.*, 1861, 118, 69; by stannous chloride, by carbon compounds, by carbon monoxide, Hargreaves and Robinson, *Ber.*, 1872, 5, 1065; by ferric chloride, Gauthier, *Annalen*, 1858, 106, 239. See also Prudhomme, *Bull. Soc. chim.*, 1903, [3], 29, 300.

<sup>8</sup> Luther and Rutter, *Zeitsch. anorg. Chem.*, 1907, 54, 1; Jabłozyński, *ibid.*, 1908, 60, 38.

stages: (a)  $\text{Cr}^{\text{VI}} \longrightarrow \text{Cr}^{\text{V}}$ ; (b)  $\text{Cr}^{\text{V}} \longrightarrow \text{Cr}^{\text{IV}}$ ; (c)  $\text{Cr}^{\text{IV}} \longrightarrow \text{Cr}^{\text{III}}$ . With hydrogen peroxide, in presence of sulphuric acid, the reaction is probably represented by the equation: <sup>1</sup>



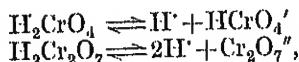
With chlorine, oxygen, ozone, or silicon, reaction is known to take place.<sup>2</sup> The liberation of iodine from an acidified solution of potassium iodide can probably be represented (assuming orthochromic acid to exist in solution) by the equation: <sup>3</sup>



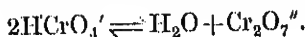
The rates of solution of different metals in solutions of chromic acid in sulphuric acid has been studied.<sup>4</sup>

Many organic compounds are readily oxidised by chromic acid.<sup>5</sup>

No hydrates of  $\text{CrO}_3$  have been obtained in the solid state.<sup>6</sup> In aqueous solution, however, they must be assumed to exist, and to possess the properties of acids. Numerous physico-chemical investigations have been carried out dealing with the nature of aqueous solutions of chromic acid,<sup>7</sup> from which it appears that the acids  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$  exist simultaneously in solution, dissociating into ions as follows:



the concentration of the intermediate ion,  $\text{HCr}_2\text{O}_7'$ , being inappreciable. The relative amounts of  $\text{HCrO}_4'$  and  $\text{Cr}_2\text{O}_7''$  present depend upon the concentration, and upon the equilibrium constant of the reaction:



In dilute aqueous solution the chief constituent is undoubtedly dichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$ , and a study of the molecular solution volumes and molecular refractivities of chromic acid, potassium chromate, and potassium dichromate affords further evidence in support of this formula for the acid.<sup>8</sup>

The products of combination of chromic acid with bases are known

<sup>1</sup> Bach, *Ber.*, 1902, 35, 872; Spitalsky, *Zeitsch. anorg. Chem.*, 1907, 56, 72; Riesensfeld and Wesch, *Ber.*, 1908, 41, 2820.

<sup>2</sup> Moissan, *Ann. Chim. Phys.*, 1885, [9], 5, 568; Lobeau, *Bull. Soc. chim.*, 1902, [3], 27, 42. See also Le Blanc, *Zeitsch. Elektrochem.*, 1901, 7, 200; Schukarow, *Zeitsch. physikal. Chem.*, 1901, 38, 353; Mooser and Eidlmann, *Ber.*, 1902, 35, 536; Luthor and Forbes, *J. Amer. Chem. Soc.*, 1900, 31, 770.

<sup>3</sup> Holblum and (Mmo.) Lew, *J. Chim. phys.*, 1912, 10, 310. See also Seubert and Christens, *Zeitsch. anorg. Chem.*, 1900, 50, 53; Moorburg, *Chem. Weekblad*, 1907, 4, 169; Gortner, *J. Physical Chem.*, 1908, 12, 632; Kernot and Pietrafesa, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii. A], 16, 275.

<sup>4</sup> van Namo and Hill, *Amer. J. Sci.*, 1910, [4], 42, 301.

<sup>5</sup> See Windaus, *Zeitsch. physiol. Chem.*, 1917, 100, 107.

<sup>6</sup> Kremann, *Monatsh.*, 1911, 32, 619; Büchner and Prins, *Zeitsch. physikal. Chem.*, 1912, 81, 113.

<sup>7</sup> Ostwald, *Zeitsch. physikal. Chem.*, 1888, 2, 78; Abegg and Cox, *ibid.*, 1904, 48, 725; Costa, *Gazzetta*, 1900, 36, i., 535; Spitalsky, *Zeitsch. anorg. Chem.*, 1907, 54, 265; Lundborg, *ibid.*, 1907, 55, 428; Hantzsch and Clark, *Zeitsch. physikal. Chem.*, 1908, 63, 307; Sherrill, *J. Amer. Chem. Soc.*, 1907, 29, 1841; Wyrnboff, *Bull. Soc. chim.*, 1900, [4], 5, 765; Dubinsky, *Compt. rend.*, 1913, 156, 1902; Margaillan, *ibid.*, 1913, 157, 994.

<sup>8</sup> Datta and Dhar, *J. Amer. Chem. Soc.*, 1916, 38, 1303.

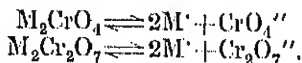
as *chromates*.<sup>1</sup> Besides normal chromates, several series of more complex salts, *e.g.* di-, tri-, and tetra-chromates, exist. These will be dealt with under the general heading.

### CHROMATES, DICHROMATES, AND POLYCHROMATES.

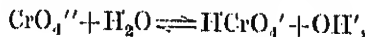
Chromates are usually yellow or red in colour, and, except those of ammonium, the alkali metals, calcium, strontium, and magnesium, are practically insoluble in water. They are obtained by oxidation of chromites,<sup>2</sup> by fusion of chromium sesquioxide with the appropriate base in presence of air or of an oxidising agent; by oxidation of chromium salts in solution; or by double decomposition.<sup>3</sup> Normal, di-, and tri-chromates, etc., are derived from one and the same acid oxide;  $K_2CrO_4$  behaves like an alkali towards  $CrO_3$ , since it is quantitatively converted into dichromate. A large number of complex double chromates are known.

Chromates, dichromates, etc., are readily reduced, *e.g.* by hydrochloric acid (with evolution of chlorine), by sulphurous acid (with formation of sulphate and dithionate),<sup>4</sup> by hydrogen sulphide (with separation of sulphur), by ferrous salts,<sup>5</sup> by alcohol,<sup>6</sup> etc., the solution simultaneously becoming green owing to the formation of a chromic salt. The chromates of the more feebly electro-positive elements decompose when strongly heated, with formation of chromium sesquioxide; dichromates of other metals yield normal chromates, chromium sesquioxide, and oxygen.<sup>7</sup>

In aqueous solution normal chromates are yellow in colour; on treatment with acid they are converted into the orange-red dichromates;<sup>8</sup> the yellow chromate is regenerated on treatment of an aqueous solution of a dichromate with an alkali. Alkali chromates and dichromates may be supposed to dissociate in solution primarily in accordance with the equations:



Chromate solutions, however, undergo hydrolysis, which may be represented thus:



<sup>1</sup> The hydrogen-ion concentrations which govern the precipitation of basic chromates have been investigated by Britton (*Trans. Chem. Soc.*, 1920, p. 125).

<sup>2</sup> Dufau, *Ann. Chim. Phys.*, 1807, [7], 12, 257; Schultze, *J. prakt. Chem.*, 1880, [2], 21, 430.

<sup>3</sup> Holzmänn, *J. prakt. Chem.*, 1858, 75, 340; Keyerband, *Zeitsch. für Chem.*, 1878, p. 525; Heinemann, *Dingl. poly. J.*, 1879, 233, 145; Fitz-Gerald, *Zeitsch. für Chem.*, 1887, p. 501; Jean, *Dingl. poly. J.*, 1869, 192, 52; Upmann, *Zeitsch. für Chem.*, 1870, p. 488; Wagner, *Dingl. poly. J.*, 1893, 277, 368; McCulloch and Donald, *Ber.*, 1878, 11, 1138; Drummond and Donald, *ibid.*, 1878, 11, 1387; Gormann, *ibid.*, 1878, 11, 1701; Pitt, *ibid.*, 1885, 18, 307; Donald, *ibid.*, 1885, 18, 307; Potter and Higgin, *ibid.*, 1885, 18, 308; Gormann, *ibid.*, 1885, 18, 307; Glöckner-Thomas, *ibid.*, 1885, 18, 308.

<sup>4</sup> Bassett, *Trans. Chem. Soc.*, 1903, 83, 602; Povornin and Chitrin, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1033.

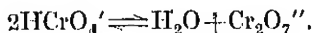
<sup>5</sup> See Forbes and Bartlett, *J. Amer. Chem. Soc.*, 1913, 35, 1527. Also Grigor, *Zeitsch. anorg. Chem.*, 1912, 76, 30; Neidle and Witt, *J. Amer. Chem. Soc.*, 1915, 37, 2300.

<sup>6</sup> Reinitzer, *Zeitsch. angew. Chem.*, 1913, 26, 450.

<sup>7</sup> See also Amadori, *Atti R. Accad. Lincei*, 1913, [5], 22, i., 600.

<sup>8</sup> For electrolytic preparation see Müller and Sauer, *Zeitsch. Elektrochem.*, 1912, 18, 844.

the hydrolysis proceeding further than would ordinarily be the case, owing to the dehydration of part of the hydrochromate ion :



Accordingly, normal chromate solutions are alkaline to the usual indicators. On the other hand, the dichromates react acid, since the dichromate ion,  $\text{Cr}_2\text{O}_7''$ , is partly hydrated, with the formation of  $2\text{HCrO}_4'$ , which in turn is slightly dissociated into  $2\text{H}^+$  and  $2\text{CrO}_4''$ . Thus, in the equilibria prevailing in chromate and dichromate solutions, the intermediate hydrochromate ion,  $\text{HCrO}_4'$ , plays an important part.<sup>1</sup>

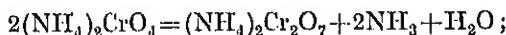
Chromates, if soluble in the gastric juices, exert a poisonous action on the human system ;<sup>2</sup> they also possess antiseptic and preservative properties.<sup>3</sup>

**Aluminium Chromate.**—The normal salt is not known. Aluminium hydroxide is soluble in chromic acid solutions,<sup>4</sup> but the nature of the mixture varies with the temperature and the concentration of the chromic acid solution.<sup>5</sup> A yellow flocculent precipitate of a basic aluminium chromate,  $\text{Al}_2\text{O}_3 \cdot \text{CrO}_3 \cdot 7\text{H}_2\text{O}$ , is produced<sup>6</sup> by adding potassium chromate to a solution of alum.

**Ammonium Chromate,**  $(\text{NH}_4)_2\text{CrO}_4$ , is formed when a solution of chromic acid is neutralised by ammonia, and the mixture evaporated. It yields golden-yellow needles (monoclinic prisms) :<sup>7</sup>

$$a : b : c = 1.9603 : 1 : 1.2226 ; \beta = 115^\circ 13',$$

of density 1.886, and soluble in water.<sup>8</sup> On heating or on exposure to air they decompose, evolving ammonia, and form the dichromate :<sup>9</sup>



consequently the chromate cannot be dried at  $100^\circ \text{C}$ . without undergoing decomposition.

A large number of double salts have been described :

**Ammonium Lithium Chromate,**  $(\text{NH}_4)\text{LiCrO}_4 \cdot 2\text{H}_2\text{O}$ , forms yellowish-brown needles.<sup>10</sup>

**Ammonium Potassium Chromate,**  $(\text{NH}_4)\text{KCrO}_4$ , is prepared by

<sup>1</sup> Sherrill, *J. Amer. Chem. Soc.*, 1907, 29, 1641 ; Abegg and Cox, *Zeitsch. physikal. Chem.*, 1904, 48, 725 ; Sand and Kaestle, *Zeitsch. anorg. Chem.*, 1907, 52, 101 ; Spitalaky, *ibid.*, 1907, 53, 184 ; 54, 265 ; Lundberg, *ibid.*, 1907, 55, 426 ; Dohn, *J. Amer. Chem. Soc.*, 1914, 36, 829. See also p. 43 on the condition of chromic acid in aqueous solution.

<sup>2</sup> Kössn, *Pflüger's Archiv*, 1902, 88, 627 ; Koenig, *Chem. Zeit.*, 1911, 35, 206 ; Anorbach and Piok, *Arbeiten Kaiserl. Gesundheitsamte*, 1913, 45, 191.

<sup>3</sup> Chamberland and Roux, *Compt. rend.*, 1883, 96, 1088 ; Miquel, *Jahresber.*, 1884, p. 1525 ; Laujarrois, *Compt. rend.*, 1877, 84, 625.

<sup>4</sup> Maus, *Pogg. Annalen*, 1827, 9, 127, 132 ; 11, 83.

<sup>5</sup> Gröger, *Ber.*, 1902, 35, 3420.

<sup>6</sup> Fairrie, *Quart. J. Chem. Soc.*, 1861, 4, 301 ; Elliot and Storer, *Proc. Amer. Acad.*, 1862, 5, 192 ; Gröger, *loc. cit.*

<sup>7</sup> Jäger and Krüss, *Ber.*, 1880, 22, 2032.

<sup>8</sup> For solubility see Schreinmakers and Filippo, *Chem. Zentr.*, 1906, i., 1321.

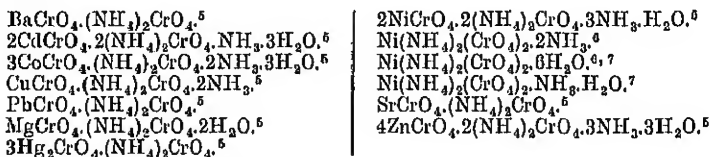
<sup>9</sup> Schreinmakers, *Chem. Zentr.*, 1905, ii., 1066 ; Ball, *Trans. Chem. Soc.*, 1909, 95, 87. See also Wyruboff, *Bull. Soc. franc. Min.*, 1879, 2, 174 ; Schröder, *Annalen*, 1874, 172, 278 ; Abbot, *Amer. J. Sci.*, 1877, [3], 14, 281 ; Sabatier, *Compt. rend.*, 1886, 103, 267 ; Pohl, *Wied. Annalen*, 1879, 6, 592 ; Schabus, *Bestimmung der Krystallgestalten*, Vienna, 1855, p. 10.

<sup>10</sup> Rammelsberg, *Pogg. Annalen*, 1866, 128, 322.

neutralising a solution of potassium dichromate with ammonia.<sup>1</sup> Also the compound,  $2(\text{NH}_4)_2\text{CrO}_4 \cdot 3\text{K}_2\text{CrO}_4$ , has been obtained<sup>2</sup> in the form of yellow needles of density 2.403 at 15° C.

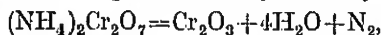
**Ammonium Sodium Chromate**,  $(\text{NH}_4)\text{NaCrO}_4 \cdot 2\text{H}_2\text{O}$ ,<sup>3</sup> crystallises in prisms of density 1.842 at 15° C.<sup>4</sup>

The following double ammonium chromates, etc., have also been described:



**Ammonium Dichromate**,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .—A solution of chromium trioxide is divided into two equal portions; one is saturated with ammonia, and the two solutions are then mixed. Ammonium dichromate separates,<sup>8</sup> after evaporation, as large garnet-red needles.

An alternative method of preparation depends<sup>9</sup> upon the interaction in aqueous solution of ammonium chloride and potassium dichromate. Ammonium dichromate is very soluble in water, and may be separated from ammonium chloride and potassium dichromate by precipitation with alcohol.<sup>10</sup> The crystals are monoclinic<sup>11</sup> (probably isomorphous with the monoclinic form of potassium dichromate),<sup>12</sup> and have<sup>13</sup> density 2.15. On heating, nitrogen is evolved (at a red heat, flame is produced), but the reaction is not so simple as that expressed by the usual equation:



since at the same time ammonia, oxides of nitrogen, and some oxygen are produced.<sup>14</sup>

The double salts  $(\text{NH}_4)_6\text{Cr}_2\text{O}_7\text{Cl}_4 \cdot 6\text{Hg}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \cdot \text{HgCl}_2$ , and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \cdot \text{Cl}_2 \cdot (\text{HgCl}_2)_4 \cdot 2\text{H}_2\text{O}$  have been prepared.<sup>15</sup> *Ammonium trichromate*,  $(\text{NH}_4)_2\text{Cr}_3\text{O}_{10}$ , and *ammonium tetrachromate*,  $(\text{NH}_4)_2\text{Cr}_4\text{O}_{13}$ , are obtained<sup>16</sup> similarly to the corresponding potassium salts. The

<sup>1</sup> Kopp, *Chem. News*, 1864, 9, 278, 290; Johnson, *J. prakt. Chem.*, 1854, 62, 201.

<sup>2</sup> Zehnter, *Monatsh.*, 1897, 18, 48.

<sup>3</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1879, 2, 174.

<sup>4</sup> Zehnter, *loc. cit.*

<sup>5</sup> Gröger, *Zeitsch. anorg. Chem.*, 1908, 58, 412.

<sup>6</sup> Briggs, *Trans. Chem. Soc.*, 1903, 83, 391.

<sup>7</sup> Gröger, *loc. cit.*, 1906, 51, 348.

<sup>8</sup> Abel, *Annalen*, 1850, 76, 251; Berthelot, *Ann. Chim. Phys.*, 1884, [6], 1, 93; Darby, *Annalen*, 1848, 65, 204.

<sup>9</sup> Segalle, *Chem. Zentr.*, 1905, ii., 444.

<sup>10</sup> Segalle, *loc. cit.*; Schreinmakers and Filippo, *Chem. Zentr.*, 1906, i., 1321.

<sup>11</sup> Prismatic;  $a : b : c = 1.0271 : 1 : 1.7665$ ;  $\beta = 93^\circ 42'$  (Rammelsberg, *Pogg. Annalen*, 1863, 118, 158).

<sup>12</sup> Hauser and Herzfeld, *Zeitsch. physikal. Chem.*, 1909, 68, 175.

<sup>13</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1890, 13, 306; Abbot, *Amer. J. Sci.*, 1877, [3], 14, 281.

<sup>14</sup> Böttger, *Annalen*, 1843, 47, 339; Segalle, *loc. cit.*; Hooton, *Proc. Chem. Soc.*, 1908, 24, 23; Frankforter, Roehrich, and Manuel, *J. Amer. Chem. Soc.*, 1910, 32, 178. See also Berthelot, *Compt. rend.*, 1883, 96, 400, 541; Gentelo, *Dingl. poly. J.*, 1851, 125, 460; Böttger, *J. prakt. Chem.*, 1868, 103, 314.

<sup>15</sup> Strömholm, *Zeitsch. anorg. Chem.*, 1912, 75, 277; 1913, 80, 155.

<sup>16</sup> Siewort, *Zeitsch. ges. Naturwiss.*, 1862, 19, 17; Jäger and Krüss, *Ber.*, 1880, 22, 2023; Wyruboff, *Bull. Soc. franç. Min.*, 1880, 3, 136; 1881, 4, 17, 120; *Bull. Soc. chim.*, 1881, [2], 35, 162; Schröder, *Jahresber.*, 1879, p. 31. See also Rammelsberg, *Pogg. Annalen*, 1855, 94, 510.

former crystallises in the rhombic <sup>1</sup> system, and has density 2.329; the latter has density 2.343, and is isomorphous with potassium tetrachromate (p. 62).

**Ammonium Fluorochromate**,  $\text{CrO}_3(\text{ONH}_4)_2$ , the compound,  $\text{NH}_4\text{CrO}_4 \cdot 2\text{Cr}(\text{OF})_2$ , ammonium chlorochromate,  $\text{CrO}_3(\text{ONH}_4)\text{Cl}$ , and chromiodate,  $\text{CrO}_3 \cdot \text{NH}_4\text{IO}_3 \cdot \text{H}_2\text{O}$ , have been described,<sup>2</sup> as also have chromates and dichromates of certain substituted ammonias.

**Barium Chromate**,  $\text{BaCrO}_4$ , is obtained as a pale yellow amorphous precipitate when a barium salt is added to a solution of an alkali chromate. If a dichromate is used, the precipitate tends to dissolve in the acid formed. It has a density of 4.3.<sup>3</sup> On heating, it darkens in colour, and if fused, it yields the crystalline form on cooling. The latter form is also obtained by heating a mixture of potassium and sodium chromates and barium chloride to a bright red heat, and allowing to cool. Greenish crystals are formed in the interior of the fused mass and can be isolated by lixiviation with boiling water.<sup>4</sup> The crystals have density 4.60, and are isomorphous with barium sulphate. They are only very slightly soluble in water, and the solubility has been determined <sup>5</sup> by conductivity measurements as follows:

Temperature " C.	0	10	20	30
Grams per litre of solution	0.002	0.0028	0.0037	0.0046

For analytical purposes the solubility has also been determined in dilute acetic acid and in solutions of ammonium salts,<sup>6</sup> and Waddell has shown that for washing barium chromate, pure water is preferable to a one per cent. ammonium acetate solution, which latter dissolves about four times as much of the salt as an equal quantity of water.

Barium chromate readily dissolves in hydrochloric and nitric acids, forming the dichromate; concentrated sulphuric acid decomposes it, forming barium sulphate and chromic acid; it also dissolves in molten sodium nitrate.<sup>7</sup> The simultaneous precipitation of barium chromate and barium carbonate, and of barium chromate and barium sulphate, has been studied.<sup>8</sup>

Barium chromate finds its way into the market as a pigment under various names, such as barium chrome, lemon chrome, and yellow ultramarine. It is very permanent, but is deficient in brightness and body, and is therefore not widely used.

Double salts of barium chromate, for example,  $\text{BaK}_2(\text{CrO}_4)_2$ ,  $\text{Ba}(\text{NH}_4)_2(\text{CrO}_4)_2$ , are obtained as light yellow precipitates <sup>9</sup> by adding

<sup>1</sup> Bipyramidal; a : b : c = 0.8440 : 1 : 0.8344.

<sup>2</sup> Varrenr, *Compt. rend.*, 1880, 91, 680; 1881, 93, 728; Péllet, *Ann. Chim. Phys.*, 1883, 52, 283.

<sup>3</sup> Schroeder, *Annalen*, 1874, 174, 240; Schafarik, *J. prakt. Chem.*, 1803, 90, 1, gives 4.40.

<sup>4</sup> Bourgeois, *Compt. rend.*, 1870, 88, 382.

<sup>5</sup> Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, 64, 120.

<sup>6</sup> Schweitzer, *Zeitsch. anal. Chem.*, 1800, 29, 414; Fresenius, *ibid.*, 29, 418; Waddell, *Analyst*, 1918, 43, 287.

<sup>7</sup> Guthrie, *J. Chem. Soc.*, 1886, 47, 94.

<sup>8</sup> Morin, *Annalen*, 1882, 213, 253; Chromatschoff and Martinoff, *Ann. Chim. Phys.*, 1887, [6], 11, 234. See also Scholtz and Alegg, *Zeitsch. Elektrochem.*, 1900, 12, 425; Tollum, *J. Chim. phys.*, 1900, 7, 280.

<sup>9</sup> Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185; 1908, 58, 412; Barro, *Compt. rend.*, 1914, 158, 495.



a large excess of the alkali chromate to a solution of a barium salt. They are decomposed by water.

**Barium Dichromate**,  $\text{BaCr}_2\text{O}_7$ , is obtained in the anhydrous condition by heating together moist barium chromate and chromium trioxide; <sup>1</sup> it crystallises in slender needles, and is decomposed by water into chromic acid and barium chromate. It is also prepared by heating a mixture of barium chloride and chromium trioxide.<sup>2</sup> The *dihydrate*,  $\text{BaCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , is obtained <sup>3</sup> by concentration of a solution of barium chromate in chromic acid; it yields yellowish-brown rhombic crystals: <sup>4</sup>

$$a : b : c = 0.5838 : 1 : 1.293.$$

On heating to  $120^\circ \text{C}$ . the crystals become anhydrous.<sup>5</sup>

**Barium Potassium Trichromate**,  $2\text{BaCr}_3\text{O}_{10} \cdot \text{K}_2\text{Cr}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ , is formed <sup>6</sup> when a potassium salt is added to a chromic acid solution of barium dichromate and the mixture concentrated; it crystallises in brownish-red needles, which are very deliquescent and are decomposed by water.

**Beryllium Chromate**,  $\text{BeCrO}_4 \cdot \text{H}_2\text{O}$ , and the basic compound,  $\text{BeCrO}_4 \cdot 6\text{Be}(\text{OH})_2$ , have been described by Glassmann,<sup>7</sup> whose results, however, have not been confirmed by subsequent workers.<sup>8</sup> It appears to be established that a solution of chromic acid absorbs beryllium hydroxide in the exact ratio of  $1\text{Be}(\text{OH})_2 : 1\text{CrO}_3$ , which points to the formation of the neutral chromate. When solutions of beryllium salts are treated with equivalent quantities of chromates, the precipitates at first formed redissolve; <sup>9</sup> but if the chromate is added in excess, yellow precipitates of strongly basic beryllium chromates of uncertain composition are obtained.

**Bismuth Chromate**.—The neutral salt is not known. The metal shows an exceptionally marked tendency to form double salts, and a very large number of basic chromates have been described. It has been shown by Cox,<sup>10</sup> however, from an investigation of the conditions under which the chromates of bismuth are capable of existing in solutions of chromic acid, that in accordance with the phase rule only two such compounds,  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  and  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ , definitely exist. The former yields orange-scarlet monoclinic prisms, decomposed by water and by heat; the latter is an orange-yellow powder, which is sometimes called *bismuthyl dichromate*,  $(\text{BiO})_2\text{Cr}_2\text{O}_7$ .

It must be assumed, therefore, that most of the basic salts described in the literature are not true compounds, or at least that they do not exist in the system  $\text{Bi}_2\text{O}_3 - \text{CrO}_3 - \text{H}_2\text{O}$ ; however, some may exist in such a system as  $\text{K}_2\text{O} - \text{Bi}_2\text{O}_3 - \text{CrO}_3 - \text{H}_2\text{O}$ ; for example, the compounds  $3\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$  and  $3\text{Bi}_2\text{O}_3 \cdot \text{CrO}_3$  appear to be stable in alkaline solutions.

**Bismuth Potassium Chromates**.—When potassium chromate, or dichromate, is added to a solution of a bismuth salt, the yellow precipitate formed, if allowed to remain in contact with the solution,

<sup>1</sup> Autenrieth, *Ber.*, 1902, 35, 2057; Preis and Rayman, *ibid.*, 1880, 13, 340; Bahr, *J. prakt. Chem.*, 1853, 60, 80.

<sup>2</sup> Mayer, *Ber.*, 1903, 36, 1740.

<sup>3</sup> Bahr, *loc. cit.*; Zettinow, *Pogg. Annalen*, 1872, 145, 167.

<sup>4</sup> Preis and Rayman, *loc. cit.*

<sup>5</sup> Zettinow, *loc. cit.*

<sup>6</sup> Bahr, *loc. cit.*

<sup>7</sup> Glassmann, *Ber.*, 1907, 40, 2002.

<sup>8</sup> Orlov, *Zeitsch. anorg. Chem.*, 1913, 79, 305; Bleyer and Moormann, *ibid.*, 1912, 76, 70.

<sup>9</sup> Bleyer and Moormann, *loc. cit.*

<sup>10</sup> Cox, *Zeitsch. anorg. Chem.*, 1906, 50, 226.

gradually darkens in colour, yielding the double salt,  $K_2O.Bi_2O_3.4CrO_3$ .<sup>1</sup> Boiling with water removes all the alkali and leaves the basic salt,  $Bi_2O_3.2CrO_3$ . On warming the double salt with a concentrated solution of chromic acid, dark red crystals of the compound,  $K_2O.Bi_2O_3.6CrO_3.H_2O$ , are formed, which likewise decompose on boiling with water.

**Cadmium Chromate**,  $CdCrO_4$ , may be obtained<sup>2</sup> by heating a solution of the dichromate with cadmium hydroxide, in a sealed tube, at  $200^\circ C.$ , when it separates as a bright orange-yellow crystalline powder. It is insoluble in water, which, when boiling, decomposes it. If the mother-liquor from the above preparation is allowed to stand for a time, it deposits crystals of the *dihydrate*  $CdCrO_4.2H_2O$ .

*Basic cadmium chromates*, e.g.  $5CdO.2CrO_3.H_2O$ , have been described.<sup>3</sup>

*Basic double salts*, e.g.  $(NH_4)_2O.4CdO.4CrO_3.3H_2O$  and  $K_2O.4CdO.4CrO_3.3H_2O$ , are formed<sup>4</sup> when an alkali chromate is added to solutions containing excess of cadmium salt; with excess of potassium chromate the double salt,  $K_2Cd(CrO_4)_2.2H_2O$ , results;<sup>5</sup> sodium chromate yields only alkali-free basic salts. Several ammoniated compounds have been described.<sup>6</sup>

**Cadmium Dichromate**,  $CdCr_2O_7.H_2O$ , is obtained by saturating a cold solution of chromic acid with cadmium carbonate, and concentrating by evaporation, when orange-brown cubic crystals<sup>7</sup> separate, which are readily soluble, without decomposition, in water.

The double salts,  $K_2Cd(Cr_2O_7)_2.2H_2O$  and  $CdCr_2O_7.2Hg(CN)_2.7H_2O$ , have been described.<sup>8</sup>

**Cadmium Trichromate**,  $CdCr_3O_{10}.H_2O$ , is obtained<sup>9</sup> by evaporation of a solution of the dichromate as a dark red, deliquescent, crystalline crust.

**Cæsium Chromate**,  $Cs_2CrO_4$ , obtained by interaction of silver chromate and cæsium chloride in boiling aqueous solution, is yellow in colour, and exists<sup>10</sup> in two crystalline forms—rhombic (bipyramidal):

$$a : b : c = 0.5640 : 1 : 0.7577 ;$$

and rhombohedral :

$$a : c = 1 : 1.2814 ; a = 72^\circ 39'.$$

It forms a double salt,  $Cs_2Mg(CrO_4)_2.6H_2O$ ,<sup>11</sup> isomorphous with the corresponding rubidium salt.

**Cæsium Dichromate**,  $Cs_2Cr_2O_7$ , forms orange-red crystals (anorthic).<sup>12</sup> **Cæsium trichromate** and **tetrachromate** have been described.<sup>13</sup>

**Calcium Chromate**,  $CaCrO_4$ , is produced industrially as a by-product in the manufacture of alkali chromates. Finely powdered

<sup>1</sup> Preis and Rayman, *Jahresber.*, 1880, p. 336.

<sup>2</sup> Schulze, *Zeitsch. anorg. Chem.*, 1895, 10, 148; Briggs, *ibid.*, 1907, 56, 246.

<sup>3</sup> Malaguti and Sarzeau, *Ann. Chim. Phys.*, 1843, [3], 9, 431.

<sup>4</sup> Gröger, *Monatsh.*, 1904, 25, 520.

<sup>5</sup> Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185.

<sup>6</sup> Gröger, *ibid.*, 1908, 58, 412; Briggs, *J. Chem. Soc.*, 1904, 85, 672; Malaguti and Sarzeau, *loc. cit.*

<sup>7</sup> Schulze, *loc. cit.*; Gröger, *Zeitsch. anorg. Chem.*, 1910, 66, 7.

<sup>8</sup> Krüss and Unger, *Zeitsch. anorg. Chem.*, 1895, 8, 46.

<sup>9</sup> Gröger, *loc. cit.*

<sup>10</sup> Chabrió, *Ann. Chim. Phys.*, 1902, [7], 26, 212; Fraprio, *Zeitsch. Kryst. Min.*, 1900, 42, 113; Schreinemakers and Meyerlingh, *Chem. Weekblad*, 1908, 5, 811.

<sup>11</sup> Briggs, *Trans. Chem. Soc.*, 1904, 85, 677; Barker, *ibid.*, 1911, 99, 1327.

<sup>12</sup> Chabrió, *loc. cit.*; Fraprio, *loc. cit.*; Schreinemakers and Meyerlingh, *loc. cit.*

<sup>13</sup> Fraprio, *loc. cit.*; Schreinemakers and Meyerlingh, *loc. cit.*

chrome iron ore is roasted with chalk yielding calcium chromate, which by treatment with an alkali sulphate is converted into insoluble calcium sulphate and the soluble alkali chromate. On a small scale it is obtained by double decomposition of calcium chloride and sodium chromate, or by neutralisation of chromic acid solution by means of calcium hydroxide. It has a limited application as a pigment.

In many of its properties calcium chromate shows considerable resemblance to calcium sulphate. It yields four hydrates,<sup>1</sup> all of which are slightly more soluble in water than the anhydride. The *dihydrate*,  $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ , exists in two forms—the  $\alpha$  form, which is monoclinic and isomorphous with gypsum, and the  $\beta$  form, which is rhombic and is the most stable of the hydrates.<sup>2</sup> The former separates as amber yellow acicular crystals when a saturated solution of the chromate, prepared at  $0^\circ \text{C}$ ., is allowed to stand at room temperatures. If the crystals are allowed to remain in contact with the solution for a few days, a darkening in colour takes place and the  $\alpha$  variety completely disappears, the  $\beta$  form being produced. The  $\beta$  crystals effloresce slowly in the air, and lose all water of crystallisation at  $100^\circ \text{C}$ . Unlike the other hydrates and the anhydride, which are all less soluble in warm water than in cold, the solubility of the  $\beta$  form increases slightly with the temperature. A saturated solution containing 10.3 per cent. of the salt at  $18^\circ \text{C}$ . has a density of 1.105.<sup>3</sup> Above  $14^\circ \text{C}$ . the *monohydrate* is more stable than the  $\beta$  dihydrate, and if a saturated solution of the latter, or of the  $\alpha$  salt, be kept at  $80^\circ \text{C}$ . for several days, the monohydrate separates in the form of rhombic crystals :<sup>4</sup>

$$a : b : c = 0.6290 : 1 : 0.6404,$$

of density 2.793 at  $15^\circ \text{C}$ . Like calcium sulphate, the chromate yields a *hemihydrate*,  $2\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ , which may be obtained by heating a 15 per cent. solution of calcium chromate with an equal volume of glycerol at  $100^\circ \text{C}$ .<sup>5</sup> It forms small octahedral crystals, which only completely lose their water at  $400^\circ \text{C}$ .

Anhydrous calcium chromate may be conveniently prepared by dehydration of any of the above hydrates at high temperatures. It is less soluble than the hydrates, and is the most stable form.<sup>6</sup> It dissolves in molten sodium nitrate.<sup>7</sup>

A few double salts obtained by double decomposition of calcium chloride with excess of concentrated solutions of alkali chromate, or by neutralisation of dichromate solutions with lime, have been described.<sup>8</sup>

A *basic calcium chromate*,  $\text{CaCrO}_4 \cdot \text{CaO} \cdot 8\text{H}_2\text{O}$ , results as large poly-

<sup>1</sup> Mylius and von Wrochem, *Ber.*, 1900, 33, 3689; von Foullon, *Jahrb. kk. geol. Reichsanst.*, 1900, p. 421.

<sup>2</sup> Most of the earlier data concerning the dihydrate probably refer to the  $\beta$  form. See Bahr, *J. prakt. Chem.*, 1853, 60, 60; Stewert, *Zeitsch. ges. Naturwiss.*, 1862, 19, 11; *Jahresber.*, 1862, p. 146; Schwarz, *Dingl. poly. J.*, 1870, 198, 160.

<sup>3</sup> Mylius and von Wrochem, *loc. cit.*

<sup>4</sup> von Foullon, *loc. cit.* See also Wyrnouboff, *Bull. Soc. franç. Min.*, 1891, 14, 203.

<sup>5</sup> Mylius and von Wrochem, *loc. cit.*

<sup>6</sup> See Kohlrausch, *Zeitsch. physikal. Chem.*, 1903, 44, 107; 1908, 64, 129; *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, p. 1218; Hosford and Jones, *Amer. Chem. J.*, 1911, 46, 240; Howard and Jones, *ibid.*, 1913, 48, 600.

<sup>7</sup> Guthrie, *J. Chem. Soc.*, 1885, 47, 64.  
<sup>8</sup> Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185; 1908, 58, 412; Schweitzer, *J. prakt. Chem.*, 1846, 39, 261; Rammelsberg, *Pogg. Annalen*, 1855, 94, 516; Wyrnouboff, *loc. cit.*; *Bull. Soc. franç. Min.*, 1900, 32, 6. Also Dimean, *Phil. Mag.*, 1850, [3], 36, 109; Bahr, *J. prakt. Chem.*, 1853, 60, 60; Barro, *Compt. rend.*, 1914, 158, 495.

hedral crystals when a solution of chromic acid supersaturated with calcium hydroxide is allowed to stand for several days.<sup>1</sup>

**Calcium Dichromate**,  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , separates in the form of reddish-brown deliquescent scales when a solution of calcium chromate in chromic acid is evaporated. On heating it becomes anhydrous and melts to a reddish-brown liquid.<sup>2</sup>

**Calcium Tetrachromate** has been said to exist.<sup>3</sup>

**Chromium Chromate** or chromium dioxide has already been described (see p. 39).<sup>4</sup>

**Cobalt Chromate**,  $\text{CoCrO}_4$ , results as a greyish-black crystalline powder when a mixture containing cobalt carbonate (12.4 grams), chromium trioxide (20 grams), and water (20 grams) is heated for four hours in a sealed tube at  $185^\circ \text{C}$ .<sup>5</sup> It is much more soluble than the corresponding nickel salt (see p. 58). The *dihydrate*  $\text{CoCrO}_4 \cdot 2\text{H}_2\text{O}$  yields bronze-coloured acicular prisms.

Basic salts are produced when cobalt salts are precipitated with sodium chromate, or when the alkali-containing double salts first produced by precipitation with ammonium or potassium chromates are subjected to continued treatment with hot water. The following double salts have been described :

$(\text{NH}_4)_2\text{Co}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$  ; <sup>6</sup>  $(\text{NH}_4)_2\text{CrO}_4 \cdot 3\text{CoCrO}_4 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$  ; <sup>7</sup>  $\text{K}_2\text{O} \cdot 4\text{CoO} \cdot 4\text{CrO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{K}_2\text{Co}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$  ; <sup>8</sup>  $\text{Cs}_2\text{Co}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ .<sup>9</sup>

**Cobalt Dichromate**,  $\text{CoCr}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , has been obtained<sup>6</sup> as black, lustrous, deliquescent crystals by heating together cobalt carbonate and chromic acid in aqueous solution at a high temperature.

The double salts,  $\text{CoCr}_2\text{O}_7 \cdot (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  and  $\text{CoCr}_2\text{O}_7 \cdot 2\text{Hg}(\text{CN})_2 \cdot 7\text{H}_2\text{O}$ , have been described.<sup>9</sup>

**Copper Chromates**.—Both cuprous<sup>10</sup> and cupric<sup>11</sup> chromates are known.<sup>12</sup> The latter forms an *ammoniacal salt*,  $2\text{CuCrO}_4 \cdot \text{CuO} \cdot 10\text{NH}_3$ , which is obtained on precipitating a green solution of basic copper chromate in ammonia by means of alcohol, as dark green needles which are unstable in air.<sup>13</sup> The salt,  $\text{CuCrO}_4 \cdot 4\text{NH}_3$ , also exists.<sup>14</sup>

Three *basic chromates* have been described : (a)  $\text{CuCrO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$ , a yellowish-brown precipitate obtained (together with some cupric dichromate) on mixing solutions of ammonium chromate and copper sulphate ; <sup>15</sup> (b)  $2\text{CuCrO}_4 \cdot 5\text{CuO} \cdot 5\text{H}_2\text{O}$  ; and (c)  $\text{CuCrO}_4 \cdot 6\text{CuO} \cdot 5\text{H}_2\text{O}$ .<sup>16</sup>

**Cupric Dichromate**,  $\text{CuCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , forms reddish-brown crystals on evaporation in the cold of a solution of cupric hydroxide in chromic acid. It becomes anhydrous at  $100^\circ \text{C}$ . It is deliquescent and soluble

<sup>1</sup> von Foulton, *loc. cit.* ; Mylius and von Wrochem, *loc. cit.*

<sup>2</sup> Vauquelin, *Ann. Chim. Phys.*, 1800, [1], 70, 70 ; Bahr, *loc. cit.*

<sup>3</sup> Mylius and von Wrochem, *loc. cit.*

<sup>4</sup> See also Britton, *Trans. Chem. Soc.*, 1926, p. 132. Chromium dichromate,  $\text{Cr}_2(\text{Cr}_2\text{O}_7)_2$ , is described by Caloganni, *Gazzetta*, 1925, 55, 300.

<sup>5</sup> Briggs, *Zeitsch. anorg. Chem.*, 1909, 63, 325.

<sup>6</sup> Briggs, *ibid.*, 1908, 56, 246.

<sup>7</sup> Gröger, *ibid.*, 1908, 58, 412.

<sup>8</sup> Gröger, *ibid.*, 1906, 49, 195.

<sup>9</sup> Krüss and Unger, *ibid.*, 1895, 8, 45.

<sup>10</sup> Porsoz, *Compt. rend.*, 1861, 53, 71.

<sup>11</sup> Gerber, *Bull. Soc. chim.*, 1877, [2], 27, 436.

<sup>12</sup> See also Briggs, *Proc. Chem. Soc.*, 1902, 18, 254 ; Parravano and Pasta, *Gazzetta*, 1907, 37, ii., 252 ; Wöhler and Wöhler, *Zeitsch. physikal. Chem.*, 1908, 62, 440.

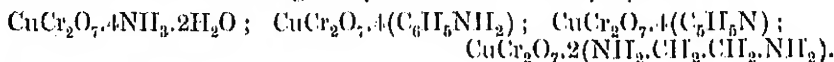
<sup>13</sup> Nussliart, *J. Pharm.*, 1824, 10, 607 ; Malaguti and Sarzeau, *Ann. Chim. Phys.*, 1843, [3], 9, 434 ; Knop, *Annalen*, 1849, 70, 52.

<sup>14</sup> Parravano and Pasta, *loc. cit.*

<sup>15</sup> Malaguti and Sarzeau, *loc. cit.* ; Fresco, *Pogg. Annalen*, 1870, 140, 87 ; Rosenfeld, *Ber.*, 1880, 13, 1460 ; Porsoz, *Ann. Chim. Phys.*, 1849, [3], 25, 283.

<sup>16</sup> Rosenfeld, *loc. cit.*

in water and alcohol. The aqueous solution on boiling yields the basic chromate.<sup>1</sup> The following compounds have been prepared :<sup>2</sup>



*Copper trichromate and tetrachromate* are also known.<sup>3</sup>

**Gold Chromates.**<sup>4</sup>—A red solution of auric chromate,  $\text{Au}_2(\text{CrO}_4)_3$ , is obtained by treating a solution of auric chloride with a large excess of freshly precipitated silver chromate. On evaporation, first metallic gold is precipitated, and then the compound  $\text{Au}_2(\text{CrO}_4)_3 \cdot \text{CrO}_3$  crystallises out.

**Indium Chromates** do not appear to have been analysed, but Meyer<sup>5</sup> has described an insoluble basic salt and a soluble, non-crystallisable acid salt.

**Iron Chromates.**—Ferrous chromate does not appear to be capable of existence. When solutions of ferrous sulphate and chromic acid, or its alkali salts, are mixed at low temperatures, the iron is oxidised, basic ferric sulphates resulting, the chromium being correspondingly reduced. If the ferrous sulphate is in excess, ferroso-ferric sulphate results.

**Ferric Chromate** has not been obtained as the normal salt, but by digesting ferric hydroxide with chromic acid, a brown amorphous substance, soluble in water and alcohol, and of composition  $\text{Fe}_2\text{O}_3 \cdot 4(\text{CrO}_3)$ , has been obtained.<sup>6</sup> By the addition of potassium chromate to a solution of a ferric salt, a brown precipitate, of composition  $\text{Fe}_2\text{O}_3 \cdot \text{CrO}_3$ , is obtained.<sup>7</sup> It is decomposed by water.

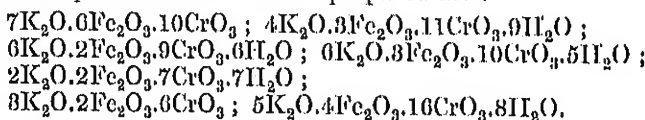
Numerous basic double ferric chromates have been prepared,<sup>8</sup> namely :

$3\text{K}_2\text{O} \cdot 6\text{Fe}_2\text{O}_3 \cdot 2\text{CrO}_3$ —obtained by the action of ferrous sulphate on potassium chromate at  $0^\circ \text{C}$ ., at which temperature it is dried with alcohol and ether. It is black in appearance, but brown when moist.

$4\text{K}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{CrO}_3$ —a yellowish-brown micro-crystalline precipitate, obtained by addition of excess of potassium chromate to ferrous sulphate solution.

$4\text{Na}_2\text{O} \cdot 7\text{Fe}_2\text{O}_3 \cdot 10\text{CrO}_3$  and  $6(\text{NH}_4)_2\text{O} \cdot 5\text{Fe}_2\text{O}_3 \cdot 6\text{CrO}_3$  are obtained in a similar manner to the preceding salt, but replacing potassium chromate by sodium and ammonium chromates respectively.

Other complexes that have been prepared are :<sup>9</sup>



**Ferric Ammonium Chromate**,  $(\text{NH}_4)_2\text{CrO}_4 \cdot \text{Fe}_2(\text{CrO}_4)_3 \cdot 4\text{H}_2\text{O}$ , and ferric potassium chromate,  $\text{K}_2\text{CrO}_4 \cdot \text{Fe}_2(\text{CrO}_4)_3 \cdot 4\text{H}_2\text{O}$ , have been prepared<sup>9</sup> as dark red crystalline plates by the slow evaporation

<sup>1</sup> Dröge, *Annalen*, 1857, 101, 30 ; Balbiano, *Gazzetta*, 1888, 18, 105 ; Gröger, *Zeitsch. anorg. Chem.*, 1910, 66, 7.

<sup>2</sup> Gröger, *loc. cit.*

<sup>3</sup> Parravano and Pasta, *Gazzetta*, 1907, 37, II, 252.

<sup>4</sup> Orloff, *Chem. Zeit.*, 1907, 31, 1182.

<sup>5</sup> Meyer, *Bull. Soc. chim.*, 1868, [2], 10, 18, 300 ; 1869, [2], 12, 232 ; *Annalen*, 1869, 150, 137.

<sup>6</sup> Maus, *Pogg. Annalen*, 1827, 9, 127, 132 ; 11, 83 ; Elliot and Storer, *Proc. Amer. Acad.*, 1861, 5, 192, 207.

<sup>7</sup> Elliot and Storer, *loc. cit.* ; Kletzensky, *Dingl. poly. J.*, 1873, 207, 83.

<sup>8</sup> Lepierre, *Compt. rend.*, 1894, 119, 1215.

<sup>9</sup> Henson, *Ber.*, 1870, 12, 1650.

of mixed solutions of ferric chloride and ammonium (or potassium) dichromate.

**Lead Chromates.**—Lead forms the normal chromate,  $\text{PbCrO}_4$ , the dichromate,  $\text{PbCr}_2\text{O}_7$ , and several basic salts.

**Normal Lead Chromate,  $\text{PbCrO}_4$ ,** occurs naturally as crocoite in Siberia, Brazil, and other parts (see p. 8); the mineral crystallises in hyacinth-red, translucent, monoclinic prisms, and has a density of about 6.0. It was prepared artificially by Bourgeois<sup>1</sup> by heating precipitated lead chromate with dilute nitric acid in sealed tubes at  $130^\circ\text{C}$ . The salt is prepared artificially as a bright yellow precipitate by mixing solutions of a lead salt and potassium chromate or dichromate. Probably the precipitate is at first amorphous, but it gradually becomes crystalline. Crystals of lead chromate are also obtained by exposing to the air a solution of the precipitated chromate in caustic soda, by fusing together lead chloride and potassium chromate, by allowing solutions of lead acetate and potassium chromate to mix slowly by diffusion,<sup>2</sup> and by electrolysing a dilute solution of chromic acid with lead electrodes.<sup>3</sup>

Precipitated lead chromate tends to change colour during filtration, becoming orange. This is due to the formation of the red basic salt,  $\text{Pb}_2\text{CrO}_5$  or  $\text{PbCrO}_4 \cdot \text{PbO}$ , by hydrolysis, which is the more likely to take place when the salt is prepared from basic lead acetate.<sup>4</sup>

Lead chromate is valued as a pigment under the names of chrome yellow, Paris yellow, and Leipzig yellow, and consequently it is important to realise the best conditions for its preparation. It has been shown<sup>5</sup> that the rapid mixing of cold, concentrated solutions of the reacting salts under conditions which prevent the formation of basic salt, produces a crystalline chrome yellow of clear colour and good covering power. Commercial chrome yellow frequently contains lead sulphate, and a pigment known as Cologne yellow is prepared by heating lead sulphate with a solution of potassium dichromate. In some cases potassium chromate is treated with sulphuric acid, or the dichromate is mixed with a sulphate, such as Glauber salt, alum, etc., and the mixture employed to precipitate a suitable quantity of sugar of lead solution.<sup>6</sup> It is recognised that the admixture of lead sulphate to the extent of about 10 per cent. produces a lighter tint; and this is due not only to a physical cause, but to the fact that the presence of a soluble lead salt reduces or prevents hydrolysis, which by producing the basic chromate would cause darkening of colour.<sup>4</sup>

The solubility of lead chromate in water is exceedingly small; indeed, the chromate is probably the least soluble salt of lead. It is practically insoluble also in dilute acetic acid; consequently chromate ions in presence of acetic acid constitute a very delicate test for lead ions in solution. The solubility of lead chromate in water at  $25^\circ\text{C}$ . is about  $10^{-4}$  grams per litre according to Kohlrausch,<sup>7</sup> but von Hevesy and Paneth<sup>8</sup> obtained the value  $1.2 \times 10^{-5}$  grams per litre by employing

<sup>1</sup> Bourgeois, *Bull. Soc. franç. Min.*, 1887, 10, 187.

<sup>2</sup> Drevermann, *Annalen*, 1853, 87, 121.

<sup>3</sup> Le Blanc and Bindschöeller, *Zeitsch. Elektrochem.*, 1902, 8, 255.

<sup>4</sup> Jabłożyński, *Chem. Ind.*, 1908, 31, 731.

<sup>5</sup> Frec, *J. Physical Chem.*, 1900, 13, 114.

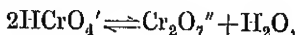
<sup>6</sup> The system  $\text{PbSO}_4 + \text{K}_2\text{CrO}_4 \rightleftharpoons \text{PbCrO}_4 + \text{K}_2\text{SO}_4$  has been investigated from the point of view of the phase rule and of chemical equilibrium by Milbauer and Kohn, *Zeitsch. physikal. Chem.*, 1910, 91, 430.

<sup>7</sup> Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, 64, 150.

<sup>8</sup> von Hevesy and Paneth, *Zeitsch. anorg. Chem.*, 1913, 82, 323.

radium-D as a *radioactive indicator*, that is, by mixing with the lead salt radium-D, which is chemically indistinguishable from lead, and estimating the radioactivity of the solution, since the original ratio between the two salts is maintained in solution.

Lead chromate readily dissolves in dilute hydrochloric and nitric acids. The solubility of this salt in dilute hydrochloric acid, and the equilibrium between chromate and dichromate in solution, have been studied.<sup>1</sup> It is found that the solubility in dilute solutions is nearly proportional to the hydrogen ion concentration, but in more concentrated solutions to the square of this value; this is attributed to the formation of dichromate ions thus :



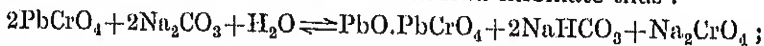
which results in more lead chromate being dissolved.

The following equilibrium constants have been calculated :

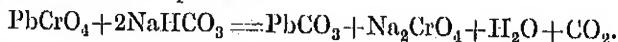
$$[\text{H}'] \cdot [\text{CrO}_4''] / [\text{HCrO}_4'] = 3.7 \times 10^{-7}; [\text{H}']^2 \cdot [\text{CrO}_4'']^2 / [\text{Cr}_2\text{O}_7''] = 3.4 \times 10^{-13};$$

$$[\text{H}'] \cdot [\text{Cr}_2\text{O}_7''] / [\text{HCr}_2\text{O}_7'] = 1.0 \times 10^{-3}; [\text{HCrO}_4']^2 / [\text{Cr}_2\text{O}_7''] = 2.5.$$

Lead chromate also dissolves in sodium hydroxide solution, being decomposed into a mixture of sodium chromate and plumbite. A solution of sodium carbonate reacts with lead chromate thus :



in presence of excess of sodium hydrogen carbonate, however, the following reaction takes place :<sup>2</sup>



Boiling with potassium nitrate solution causes lead chromate to pass into the colloidal state.<sup>3</sup>

Besides its use as a pigment, lead chromate is employed for dyeing or printing on calico. The process, which is a mechanical one, is carried out by passing the fabric first through a solution of lead salt and then through a solution of chromate. The material may, however, be agitated with precipitated lead chromate suspended in water, alcohol, or benzene. When the two latter media are employed the colour is not so deep as when water is used.<sup>4</sup>

Lead chromate fuses when strongly heated, forming a brown liquid, which on cooling solidifies to a light brown crystalline mass. At a high temperature the salt evolves oxygen, and, on account of its oxidising property, it is employed in organic analysis to aid the combustion of substances containing the elements chlorine and sulphur, which are retained by the lead. A mixture of asbestos and lead chromate may be used for absorption of sulphur compounds.<sup>5</sup>

**Basic Lead Chromates.**—The basic salt,  $\text{Pb}_2\text{CrO}_6$ ,  $\text{PbCrO}_4 \cdot \text{PbO}$ , or  $2\text{PbO} \cdot \text{CrO}_3$ , is formed as a red powder by the action of cold caustic soda solution on the normal chromate. It is also produced by mixing together lead chromate and oxide in presence of water, and is known commercially by various names—chrome red, orange chrome, Derby red, Chinese red—according to its depth of colour. It is converted by

<sup>1</sup> Beek and Stegmüller, *Arbeiten Kaiserl. Gesundheitsamte*, 1910, 34, 440.

<sup>2</sup> Auerbach and Pick, *ibid.*, 1913, 45, 166.

<sup>3</sup> de Coninck, *Bull. Acad. roy. Belg.*, 1909, p. 605.

<sup>4</sup> Vignon, *Compt. rend.*, 1909, 148, 1329; *Bull. Soc. chim.*, 1909, [4], 5, 676.

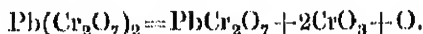
<sup>5</sup> Binder, *Chem. Zeit.*, 1918, 42, 522.

acetic acid into the normal salt, and the two salts are in equilibrium <sup>1</sup> in contact with an aqueous solution of  $2 \times 10^{-5}$  molecules  $\text{CrO}_3$  per litre at  $25^\circ \text{C}$ . Mixtures of the two salts produce tints intermediate between yellow and red; such mixtures are known commercially.

The basic salt,  $\text{Pb}_3\text{Cr}_2\text{O}_9$ , occurs in dark red hexagonal prisms, of density 5.75, as the mineral phœnicite or phœnicochroite (see p. 8). This compound may be prepared artificially by allowing solutions of lead nitrate and potassium chromate to mix by diffusion,<sup>2</sup> by exposing a solution of lead chromate in caustic potash to the air for several months,<sup>3</sup> or by immersing galena in potassium dichromate solution for six months. This last process, which was carried out by Mounier,<sup>4</sup> probably nearly reproduces the conditions by which the mineral is naturally produced.

*Double salts* of lead chromate with alkali chromates have been obtained.<sup>5</sup> The potassium salt,  $\text{K}_2\text{CrO}_4 \cdot \text{PbCrO}_4$  or  $\text{K}_2\text{Pb}(\text{CrO}_4)_2$ , is formed as a yellow amorphous precipitate when 50 c.c. of a saturated solution of potassium chromate is mixed with 10 c.c. of saturated lead acetate solution. The ammonium salt,  $(\text{NH}_4)_2\text{Pb}(\text{CrO}_4)_2$ , is prepared similarly, and both salts are decomposed into their components by water.

**Lead Dichromate**,  $\text{PbCr}_2\text{O}_7$ , containing 2 molecules of water of crystallisation, was described by Preis and Rayman,<sup>6</sup> but its existence was subsequently denied.<sup>7</sup> When a very concentrated solution of chromic acid (130 grams  $\text{CrO}_3$  per 100 c.c.) is electrolysed with a lead anode, a solution is obtained<sup>8</sup> which evolves oxygen when kept, and deposits reddish-brown needles of lead dichromate,  $\text{PbCr}_2\text{O}_7$ . From the volume of oxygen evolved it appears that plumbic dichromate is formed and decomposes thus :



Mayer obtained<sup>9</sup> lead dichromate by heating lead acetate with chromic anhydride and concentrated nitric acid under a reflux condenser; and Cox<sup>1</sup> prepared the same salt by taking account of the fact that it is prone to hydrolysis and can only be formed in contact with a chromic acid solution of a certain concentration, which is 0.805 gram-molecules  $\text{CrO}_3$  per litre at  $25^\circ \text{C}$ . Thus by grinding together lead monoxide and chromium trioxide in saturated solution in the proportion of 2 gram-molecules of the former to 5 of the latter, lead dichromate is produced and may be obtained pure after washing with 7N solution of  $\text{CrO}_3$ . It is a lustrous, red, crystalline powder.

**Lithium Chromate**,  $\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$ , forms slightly soluble<sup>10</sup> reddish-brown rhombic prisms :<sup>11</sup>

$$n : b : c = 0.602 : 1 : 0.446.$$

The following *double chromates* have been described :  $\text{LiNa}_3(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$  (ditrigonal, bipyramidal), and  $(\text{NH}_4)\text{LiCrO}_4$  (yellowish-brown needles).<sup>11</sup>

<sup>1</sup> Cox, *Zeitsch. anorg. Chem.*, 1900, 50, 226.

<sup>2</sup> Dörmann, *Annalen*, 1853, 87, 121.

<sup>3</sup> Lüdeking, *Amer. J. Sci.*, 1892, [3], 44, 57.

<sup>4</sup> Mounier, *Compt. rend.*, 1878, 87, 650.

<sup>5</sup> Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185; 1908, 58, 412; Barro, *Compt. rend.*, 1914, 158, 495.

<sup>6</sup> Preis and Rayman, *Ber.*, 1880, 13, 340.

<sup>7</sup> Autenrieth, *ibid.*, 1902, 35, 2057.

<sup>8</sup> Ellis and Nübling, *Zeitsch. Elektrochem.*, 1903, 9, 770.

<sup>9</sup> Mayer, *Ber.*, 1903, 36, 1740.

<sup>10</sup> Mylius and Funk, *ibid.*, 1897, 30, 1718; Schreinemakers, *Chem. Zentr.*, 1906, ii., 1480; Schreinemakers and Filippo, *ibid.*, 1906, i., 1321.

<sup>11</sup> Rammelsberg, *Pogg. Annalen*, 1866, 128, 311.



**Lithium Dichromate**,  $\text{Li}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , forms dark brown, almost black crystals, fairly soluble in water.<sup>1</sup>

**Lithium Chlorochromate**,  $\text{LiClCrO}_3$ , forms monosymmetric crystals.<sup>2</sup> A chromoiodate,  $\text{LiCrO}_3 \cdot \text{IO}_3 \cdot \text{H}_2\text{O}$ , has also been described.

**Magnesium Chromates.**—The *heptahydrate*,  $\text{MgCrO}_4 \cdot 7\text{H}_2\text{O}$ , is formed when a solution of chromic acid is neutralised with magnesium oxide, and the resulting solution concentrated and allowed to crystallise at ordinary temperatures. It yields yellow transparent prisms,<sup>3</sup> rhombic,<sup>4</sup> and isomorphous with the sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , with which it forms mixed crystals.<sup>5</sup> Density = 1.761<sup>6</sup> at 18° C. The crystals are very soluble in water: 100 grams of water at 18° C. dissolve 772.3 grams of  $\text{MgCrO}_4$ , the density at saturation being 1.422.<sup>8</sup>

The *pentahydrate*,  $\text{MgCrO}_4 \cdot 5\text{H}_2\text{O}$ , results<sup>9</sup> when crystallisation takes place above 30° C., or when the heptahydrate is exposed to the air for some time. It forms large yellow transparent crystals, of density 1.954,<sup>9</sup> and isomorphous with copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . On heating to 120° C. it loses water and yields the *dihydrate*,  $\text{MgCrO}_4 \cdot 2\text{H}_2\text{O}$ , from which the remaining water is only expelled on decomposition. The anhydrous salt has not been obtained.

*Double salts* of magnesium chromate with alkali chromates may be obtained by mixing solutions containing the two components in suitable proportions, or by neutralising a solution of the alkali dichromate with magnesium oxide or carbonate. Yellow crystals separate on evaporation. In the case of *ammonium*, *cesium*, and *rubidium*, isomorphous crystals of the general formula,  $\text{R}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , are obtained, isomorphous also with the corresponding double sulphates.<sup>10</sup> The corresponding *potassium* salt,  $\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , is formed only at low temperatures,<sup>11</sup> the *dihydrate*,  $\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ , being the stable form at ordinary temperatures.<sup>12</sup> The *sodium* salt,  $\text{Na}_2\text{Mg}(\text{CrO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,<sup>13</sup> becomes anhydrous at 200° C.

**Magnesium Dichromate** has not been prepared.

**Manganese Chromates.**—The normal salts have not been isolated. When an alkali chromate is added to a solution of a manganese salt, some of the manganese undergoes oxidation, and the brownish-black

<sup>1</sup> Rammelsberg, *Pogg. Annalen*, 1866, 128, 311; Schulerud, *J. prakt. Chem.*, 1870, [2], 19, 36; Schreinemakers, *Chem. Zentr.*, 1905, ii., 1486; Schreinemakers and Filippo, *ibid.*, 1906, i., 1321.

<sup>2</sup> Löwenthal, *Zeitsch. anorg. Chem.*, 1894, 6, 355; giving crystallographic data.

<sup>3</sup> Vauquelin, *Ann. Chim. Phys.*, 1809, [1], 70, 70.

<sup>4</sup> Grailich, *Sitzungsber. K. Akad. Wiss. Wien*, 1857, 27, 175. See also Grailich and Lang, *ibid.*, 1857, 27, 21; Töpsöe and Christiansen, *Ann. Chim. Phys.*, 1874, [5], 1, 21, 30.

<sup>5</sup> Fock, *Zeitsch. Kryst. Min.*, 1880, 4, 583; Dufet, *Compt. rend.*, 1884, 99, 992.

<sup>6</sup> Abbot, *Amer. J. Sci.*, 1877, [3], 14, 281. See also Boudeler, *Jahresber.*, 1880, p. 17.

<sup>7</sup> Mylius and Funk, *Ber.*, 1897, 30, 1718.

<sup>8</sup> For other data concerning magnesium-chromate solutions, see Heydwoiller, *Ann. Phys.*, 1912, [4], 37, 739; Slotte, *Wied. Annalen*, 1881, 14, 12; Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

<sup>9</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1889, 12, 69.

<sup>10</sup> Malaguti and Sarzeau, *Ann. Chim. Phys.*, 1843, [3], 9, 431; Grailich, *loc. cit.*; Briggs, *J. Chem. Soc.*, 1904, 85, 677; Gröger, *Zeitsch. anorg. Chem.*, 1908, 58, 412; Tutton and Porter, *Zeitsch. Kryst. Min.*, 1912, 51, 53.

<sup>11</sup> Briggs, *loc. cit.*

<sup>12</sup> Thomson, *Phil. Trans.*, 1827, 117, 190; von Hauer, *Sitzungsber. K. Akad. Wiss. Wien*, 1860, 39, 439; Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185; Wyruboff, *Bull. Soc. franç. Min.*, 1891, 14, 203; Abbot, *Amer. J. Sci.*, 1877, [3], 14, 281.

<sup>13</sup> Stanley, *Chem. News*, 1886, 54, 194.

precipitate formed, in addition to manganous and manganic chromates, is liable to contain <sup>1</sup> manganate and permanganate, and trivalent chromium. If the reaction takes place in the cold, the alkali metal is found in the precipitate, but this can generally be removed at boiling temperature—most readily in the case of sodium.

The existence of most of the double salts which have been described in the literature must be considered as extremely doubtful, but by adding manganous chloride to a concentrated solution of potassium chromate, *potassium manganese chromate*,  $K_2Mn(CrO_4)_2 \cdot 2H_2O$ , has been obtained by Gröger <sup>1</sup> as a red crystalline precipitate.

**Manganese Dichromate** is not known.<sup>2</sup>

**Mercury Chromates.**—*Mercurous chromate*,  $Hg_2CrO_4$ , is obtained <sup>3</sup> in the crystalline form as glittering red leaflets, when the amorphous precipitate produced by adding potassium dichromate to a solution of a mercurous salt is dissolved in boiling 5N nitric acid and the solution allowed to cool. It is also formed by adding potassium chromate to a solution of mercurous nitrate;<sup>4</sup> the yellowish-brown amorphous precipitate first formed is unstable, and changes—without change of composition—into the crystalline form, the colour of which varies from yellow to bright red, depending on the fineness of the particles. The salt is not decomposed by water in the cold; it is converted by ammonia into the chromate of Millon's Base,  $(OHg_2NH_2)_2CrO_4$ . The formation of mercurous chromate affords a useful means of estimating chromium gravimetrically (see p. 107).

*Basic salts* have been described.<sup>4</sup> By boiling the normal salt with water, or by treating the freshly formed amorphous precipitate with excess of mercurous nitrate solution, the salt,  $Hg_6Cr_2O_{10}$ , or  $2Hg_2CrO_4 \cdot Hg_2O$ , results. If, during the gradual transition of the normal salt from the amorphous to the crystalline form, water is added so that hydrolysis occurs, the salt,  $Hg_8Cr_3O_{15}$ , or  $3Hg_2CrO_4 \cdot Hg_2O$ , is produced. The basic salt,  $Hg_6CrO_6$ , or  $Hg_2CrO_4 \cdot 2Hg_2O$ , has been stated <sup>5</sup> to result from the action of sodium hydroxide on the normal chromate, but this is denied by Fichter and Oesterheld, who maintain that the mercurous oxide formed is uncombined with chromate.

The double salt,  $K_2Hg_2(CrO_4)_2$ , has been described by Gröger,<sup>6</sup> who obtained it as golden yellow non-crystalline spangles containing absorbed potassium chromate, by adding a solution of mercurous nitrate to a concentrated solution of potassium chromate. Water decomposed it, giving a basic salt.

**Mercuric Chromate**,  $HgCrO_4$ , is formed by heating an equivalent mixture of mercuric oxide and chromic anhydride with a little water.<sup>7</sup> It yields dark red rhombic prisms, which are decomposed by water with formation of the *basic salt*,  $3HgO \cdot CrO_3$ . Many basic salts have been described, but it has been shown <sup>8</sup> from an investigation of the system,  $HgO-CrO_3-H_2O$ , that the above is the only one which exists as a separate chemical entity.<sup>9</sup> It may also be produced by precipitation of

<sup>1</sup> Gröger, *Zeitsch. anorg. Chem.*, 1905, 44, 453.      <sup>2</sup> Gröger, *ibid.*, 1910, 66, 7.

<sup>3</sup> Freese, *Ber.*, 1867, 2, 478; *Pogg. Annalen*, 1870, 140, 80, 251.

<sup>4</sup> Fichter and Oesterheld, *Zeitsch. anorg. Chem.*, 1912, 76, 347.

<sup>5</sup> P. and M. M. Richter, *Ber.*, 1882, 15, 1480.

<sup>6</sup> Gröger, *loc. cit.*, 1907, 54, 185.

<sup>7</sup> Genther, *Annalen*, 1858, 106, 230.

<sup>8</sup> Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 146; 1906, 50, 226.

<sup>9</sup> Compare bismuth and lead, pp. 48 and 53.

mercuric nitrate solution with a dichromate, or by boiling mercuric oxide with potassium dichromate solution.<sup>1</sup> The compound,  $2\text{HgCrO}_4 \cdot \text{HgS}$ , formed by the action of a chromic acid solution of mercuric oxide on freshly precipitated mercuric sulphide, has explosive properties.

Mercuric Dichromate,  $\text{HgCr}_2\text{O}_7$ , is obtained as a light orange powder from a solution of the chromate in chromic acid, the concentration of the solution at  $25^\circ \text{C}$ . being greater than  $10 \cdot 46$  gram-molecules of chromic acid per litre.<sup>2</sup> It forms deep carmine-red crystals.

The compounds,  $\text{Hg}(\text{NH}_3)_2\text{CrO}_4 \cdot \text{H}_2\text{O}$  and  $(\text{OHg}_2\text{NH}_2)\text{Cr}_2\text{O}_7 \cdot 3(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , have been described,<sup>3</sup> as also have compounds with pyridine<sup>4</sup> and the double salt,  $2\text{NH}_2\text{HgCl} \cdot \text{HgCrO}_4$ .<sup>5</sup>

Nickel Chromate,  $\text{NiCrO}_4$ , is prepared in an analogous manner to the cobalt salt (see p. 51), the mixture being heated to  $260^\circ \text{C}$ .<sup>6</sup> It yields lustrous black crystals, insoluble in water and only difficultly soluble in acids. The salt is not obtained by double decomposition of a nickel salt with an alkali chromate, this reaction producing double salts of nickel chromate, the stability of which increases in the order, *potassium, rubidium, ammonium, caesium*,<sup>7</sup> and of which the general formula is  $\text{M}_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , where M is the alkali metal. The potassium salt yields mixed crystals with the analogous sulphate,  $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The *dihydrate*,  $\text{K}_2\text{Ni}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ , forms yellow crystalline needles.

Nickel Dichromate,  $\text{NiCr}_2\text{O}_7 \cdot 1 \cdot 5\text{H}_2\text{O}$ , has been prepared<sup>4</sup> by boiling a mixture of nickel carbonate and chromic acid in aqueous solution; it crystallises in reddish-brown transparent prisms, which are deliquescent. It readily forms addition compounds with organic bases; for example, pyridine yields  $\text{NiCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$ . The double salt,  $\text{NiCr}_2\text{O}_7 \cdot 2\text{Hg}(\text{CN})_2 \cdot 7\text{H}_2\text{O}$ , has been described.<sup>8</sup> Nickel trichromate has only been obtained in the amorphous condition.<sup>9</sup>

Platinum Chromates are not known.

Potassium Chromate,  $\text{K}_2\text{CrO}_4$ , is usually prepared from the dichromate (*vide infra*) by neutralisation of the excess of  $\text{CrO}_3$  above that necessary to form the normal salt, *e.g.* by potassium carbonate in aqueous solution;<sup>10</sup> by fusion of the dichromate with potassium nitrate or potassium carbonate, and extraction with water;<sup>11</sup> by interaction of potassium dichromate with ammonium chloride or sodium hydrogen phosphate.<sup>12</sup>

Potassium chromate is yellow in colour, and crystallises in the rhombic system (bipyramidal):

$$a : b : c = 0 \cdot 5694 : 1 : 0 \cdot 7298,^{13}$$

<sup>1</sup> Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 388.

<sup>2</sup> Cox, *Zeitsch. anorg. Chem.*, 1906, 50, 226.

<sup>3</sup> Hensgen, *Rec. Trav. chim.*, 1886, 5, 187.

<sup>4</sup> Briggs, *Zeitsch. anorg. Chem.*, 1908, 56, 246.

<sup>5</sup> Jäger and Krüss, *Ber.*, 1889, 22, 2028.

<sup>6</sup> Briggs, *Zeitsch. anorg. Chem.*, 1909, 63, 325.

<sup>7</sup> Briggs, *Trans. Chem. Soc.*, 1903, 83, 391; 1904, 85, 677; Gröger, *Zeitsch. anorg. Chem.*, 1906, 51, 348; 1908, 58, 412.

<sup>8</sup> Krüss and Unger, *Zeitsch. anorg. Chem.*, 1895, 8, 45.

<sup>9</sup> Gröger, *ibid.*, 1910, 66, 7.

<sup>10</sup> See Marle, *Trans. Chem. Soc.*, 1900, 95, 1492.

<sup>11</sup> Kletzensky, *Zeitsch. Chem.*, 1866, p. 209.

<sup>12</sup> Étard, *Compt. rend.*, 1877, 85, 443; Borthelot, *ibid.*, 1885, 100, 209.

<sup>13</sup> Mitscherlich, *Pogg. Annalen*, 1830, 18, 169; Brooke, *Ann. Phil.*, 1823, 22 [= [2], 6], 120.

and is isomorphous with potassium sulphate. It has a density <sup>1</sup> of 2.741, a specific heat of 0.189,<sup>2</sup> and melts at 971° C. The solid exists in two crystalline modifications, the  $\alpha$  form being stable above, and the  $\beta$  form stable below, a transition temperature of 666° C.<sup>3</sup>

The solubility of potassium chromate in water is as follows : <sup>4</sup>

Temperature, ° C.	Grams $K_2CrO_4$ in 100 Grams Water.
-11.85	54.54
0	57.11
30	65.13
60	74.60
105.8	88.8

The following table gives the results obtained by earlier workers : <sup>5</sup>

Temperature, ° C.	Grams $K_2CrO_4$ in 100 Grams Water.		
	Étard.	Alluard.	Nordenskjöld and Lindström.
0	58.2	59.3	60.2
10	60.0	61.2	62.5
20	61.7	63.2	64.5
30	63.4	65.2	66.5
40	65.2	67.0	68.6
50	66.8	69.0	70.6
60	68.6	71.0	72.7
70	70.4	73.0	74.8
80	72.1	75.0	76.9
90	73.0	77.0	79.0
100	75.6	79.0	82.2

The aqueous solution of potassium chromate has a sharp metallic taste, is poisonous, and exhibits an alkaline reaction. The freezing-point of a saturated solution is -11.86° C.,<sup>6</sup> and the boiling-point 105.8° C. Potassium chromate is soluble in solutions of potassium

<sup>1</sup> Gossner, *Zeitsch. Kryst. Min.*, 1904, 39, 163. Other values are given by Kopp, *Annalen Suppl.*, 1804, 3, 203; Schroeder, *Annalen*, 1874, 172, 270; Spring, *Ber.*, 1882, 15, 1040.

<sup>2</sup> Kopp, *loc. cit.*; Regnault's figure is 0.1851.

<sup>3</sup> Grosshuff, *Zeitsch. anorg. Chem.*, 1908, 58, 102. See also Annadori, *Atti R. Accad. Lincei*, 1913, [5], 22, i., 453, who gives melting-point = 978° C.

<sup>4</sup> Koppel and Blumenthal, *Zeitsch. anorg. Chem.*, 1907, 53, 202.

<sup>5</sup> Étard, *Ann. Chim. Phys.*, 1804, [7], 2, 550; Nordenskjöld and Lindström, *Pogg. Annalen*, 1869, 136, 314; Alluard, *Compt. rend.*, 1864, 59, 500; *Jahresber.*, 1864, p. 64. For other data for aqueous solutions and for mixtures of potassium chromate with other compounds, see de Coppot, *Ann. Chim. Phys.*, 1872, [4], 25, 536; *Zeitsch. physikal. Chem.*, 1807, 22, 230; Schiff, *Annalen*, 1859, 110, 74; 109, 320; Kromers, *Pogg. Annalen*, 1855, 96, 63; Guthrie, *Phil. Mag.*, 1875, [4], 49, 267; Fouqué, *Compt. rend.*, 1867, 64, 121; Viorodt, *Ber.*, 1872, 5, 34; Raoult, *Compt. rend.*, 1878, 87, 167; Krüss, *Ber.*, 1882, 15, 1243; de Vries, *Rec. Trav. chim.*, 1884, 3, 375; Sabatier, *Compt. rend.*, 1880, 103, 40; Schreinmakers, *Zeitsch. physikal. Chem.*, 1906, 55, 71; Schreinmakers and Filippo, *Chem. Zentr.*, 1906, i., 1321; Schreinmakers and Mooringh, *Chem. Weekblad*, 1908, 5, 811.

<sup>6</sup> Koppel and Blumenthal, *loc. cit.*

sulphate; <sup>1</sup> it is insoluble in alcohol. Its solution is readily reduced by the usual agents <sup>2</sup> on treatment with weak acids, with ammonium chloride, or with certain other salts. <sup>3</sup>

*Double Salts.*—Potassium chromate combines with various chromates and other salts to form double salts. Those which have been described in the literature are as follows :

$K_2CrO_4 \cdot Na_2CrO_4$ . <sup>4</sup>	$K_2Mg(CrO_4)_2 \cdot 6H_2O$ . <sup>15</sup>
$3K_2CrO_4 \cdot Na_2CrO_4$ . <sup>5</sup>	$K_2Zn(CrO_4)_2 \cdot 2H_2O$ . <sup>13</sup>
$KCu_2(OH)(CrO_4)_2 \cdot H_2O$ . <sup>6</sup>	$K_2CrO_4 \cdot 3ZnCrO_4 \cdot ZnO \cdot 3H_2O$ . <sup>14</sup>
$KCu_2(CrO_4)_2 \cdot 2NH_3$ . <sup>7</sup>	$K_2CrO_4 \cdot 2ZnCrO_4 \cdot 2ZnO \cdot 3H_2O$ . <sup>14</sup>
$K_2CrO_4 \cdot 2CuCrO_4 \cdot CuO \cdot 2H_2O$ . <sup>8</sup>	$K_2Cd(CrO_4)_2 \cdot 2H_2O$ . <sup>13</sup>
$K_2Ca(CrO_4)_2$ . <sup>9</sup>	$K_2CrO_4 \cdot 2CdCrO_4 \cdot CdO \cdot 2H_2O$ . <sup>15</sup>
$K_2Ca(CrO_4)_2 \cdot 2H_2O$ . <sup>10</sup>	$K_2Hg_2(CrO_4)_2$ . <sup>13</sup>
$K_2CrO_4 \cdot 5CaCrO_4$ . <sup>11</sup>	$K_2Pb_2(CrO_4)_2$ . <sup>13</sup>
$K_2CrO_4 \cdot 4CaCrO_4 \cdot 2H_2O$ . <sup>10</sup>	$K_2Yb_2(CrO_4)_2 \cdot Yb(OH)_3 \cdot 1.5 \cdot 5H_2O$ . <sup>16</sup>
$K_2CrO_4 \cdot CaCrO_4 \cdot H_2O$ . <sup>12</sup>	$K_2CrO_4 \cdot 2(UO_2)CrO_4 \cdot 6H_2O$ . <sup>17</sup>
$2K_2CrO_4 \cdot CaCrO_4$ . <sup>12</sup>	$K_2CrO_4 \cdot 2MnCrO_4 \cdot 4H_2O$ . <sup>18</sup>
$K_2CrO_4 \cdot Na_2CrO_4 \cdot CaCrO_4 \cdot H_2O$ . <sup>12</sup>	$K_2CrO_4 \cdot Fe_2(CrO_4)_3 \cdot 4H_2O$ . <sup>10</sup>
$K_2Sr(CrO_4)_2$ . <sup>13</sup>	$K_2CrO_4 \cdot CoCrO_4 \cdot 2H_2O$ . <sup>20</sup>
$K_2Sr(CrO_4)_2 \cdot 2H_2O$ . <sup>13</sup>	$K_2CrO_4 \cdot NiCrO_4 \cdot 2H_2O$ . <sup>21</sup>
$K_2Ba(CrO_4)_2$ . <sup>13</sup>	$K_2CrO_4 \cdot NiCrO_4 \cdot 6H_2O$ . <sup>15</sup>
$K_2Ba(CrO_4)_2 \cdot 2H_2O$ . <sup>13</sup>	$K_2CrO_4 \cdot (NH_4)_2CrO_4$ . <sup>22</sup>
$K_2Mg(CrO_4)_2 \cdot 2H_2O$ . <sup>14</sup>	

In some cases these double chromates are referred to under the various metals in other volumes in the series.

Doubtless some of the above, on reinvestigation, would not be proved to exist as definite compounds. Potassium chromate also forms a compound, <sup>23</sup>  $2K_2CrO_4 \cdot 3Hg(CN)_2 \cdot 2H_2O$ .

<sup>1</sup> von Hauer, *J. prakt. Chem.*, 1868, 103, 118; Rammelsberg, *Pogg. Annalen*, 1854, 91, 353; Groth, *ibid.*, 1868, 133, 193.

<sup>2</sup> Döpping, *Annalen*, 1843, 46, 172; Berthier, *Ann. Chim. Phys.*, 1843, [3], 7, 77. For other reactions see Guthrie, *Phil. Mag.*, 1884, [5], 17, 462; Stammer, *Patent-Blatt*, 82, 135; Thomas, *J. Chem. Soc.*, 1878, 33, 371; Bassott, *ibid.*, 1903, 83, 692; Brunck, *Annalen*, 1904, 336, 281; Müller and Sauer, *Zeitsch. Elektrochem.*, 1912, 18, 844.

<sup>3</sup> Schweitzer, *J. prakt. Chem.*, 1855, 65, 173; Marguerite, *J. Pharm.*, 1855, [3], 27, 21; Woodcock, *J. Chem. Soc.*, 1871, [2], 9, 785; Mohr, *Zeitsch. anal. Chem.*, 1872, 11, 278; Meyers, *Ber.*, 1873, 6, 141.

<sup>4</sup> von Hauer, *J. prakt. Chem.*, 1861, 83, 359; Rose, *Pogg. Annalen*, 1841, 52, 585.

<sup>5</sup> Flach, *Jahrb. Miner.*, 1913, i., Ref. 212.

<sup>6</sup> Briggs, *Trans. Chem. Soc.*, 1904, 85, 672.

<sup>7</sup> Knop, *Annalen*, 1849, 70, 52; Gerhardt, *J. Pharm.*, 1847, [3], 12, 57; Rosenfeld, *Ber.*, 1880, 13, 1460.

<sup>8</sup> Schweitzer, *J. prakt. Chem.*, 1846, 39, 261; Rammelsberg, *Pogg. Annalen*, 1855, 94, 517; Schroeder, *Jahresber.*, 1879, p. 31; Rakowski, *Bull. Acad. Sci. Petrograd*, 1908, 10, 905; Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185.

<sup>9</sup> Bahr, *J. prakt. Chem.*, 1853, 60, 60; Duncan, *ibid.*, 1850, 50, 54; Rammelsberg, *Pogg. Annalen*, 1850, 98, 507.

<sup>10</sup> Hannay, *Trans. Chem. Soc.*, 1877, 23, 99.

<sup>11</sup> Thomson, *Phil. Trans.*, 1827, 117, 224; Gröger, *loc. cit.*; Barro, *loc. cit.*

<sup>12</sup> Prüssen and Philippona, *Annalen*, 1869, 149, 92.

<sup>13</sup> Briggs, *Trans. Chem. Soc.*, 1904, 85, 677; Duffour, *Compt. rend.*, 1919, 169, 73; *Bull. Soc. franç. Min.*, 1919, 42, 247; *Chem. Zentr.*, 1920, i., 726; Preis and Rayman, *Jahresber.*, 1880, p. 336.

<sup>14</sup> Cleve, *Zeitsch. anorg. Chem.*, 1902, 32, 129.

<sup>15</sup> Hensgen, *Rec. Trav. chim.*, 1885, 4, 212.

<sup>16</sup> Gröger, *Zeitsch. anorg. Chem.*, 1900, 49, 195.

<sup>17</sup> Berthier, *Ann. Chim. Phys.*, 1843, [3], 7, 77; Johnson, *J. prakt. Chem.*, 1850, 50, 54.

<sup>18</sup> Strömholm, *Zeitsch. anorg. Chem.*, 1913, 80, 155.

<sup>19</sup> Formánek, *Annalen*, 1800, 257, 108.

<sup>20</sup> Hensgen, *Ber.*, 1870, 12, 1300, 1656.

<sup>21</sup> Gröger, *ibid.*, 1906, 51, 348.

**Potassium Dichromate**,  $K_2Cr_2O_7$ , may be prepared from the sodium salt and potassium chloride,<sup>1</sup> or by a direct method. In the latter case, chrome iron ore (p. 7) is calcined in the air with calcium carbonate, and the mass extracted with water containing a little sulphuric acid. Potassium carbonate is then added, and, after filtration and addition of sulphuric acid, the potassium dichromate is separated by fractional crystallisation.<sup>2</sup> An alternative method consists in heating *chromite* with calcium carbonate and potassium sulphate, and lixiviating the mass with water.<sup>3</sup> Oxidation of chromite by means of fused potassium nitrate is sometimes convenient, especially upon a small scale. Potassium dichromate is formed by the addition of any acid to a solution of potassium chromate (see p. 44).<sup>4</sup>

Dark orange in colour, potassium dichromate exists in two crystalline forms, the stable form belonging, apparently, to the asymmetric class of the triclinic system :

$$a : b : c = 0.5575 : 1 : 0.5511 ; \alpha = 82^\circ 0' ; \beta = 90^\circ 51' ; \gamma = 83^\circ 47'.^5$$

An unstable monoclinic form, isomorphous with rubidium and ammonium dichromates, has been obtained<sup>6</sup> admixed with the triclinic variety, by concentrating, after filtration from aluminium hydroxide, a mixture of potassium chromate and aluminium sulphate, and allowing the solution to crystallise. It may also be obtained in yellowish brown, doubly refracting monoclinic plates by crystallisation of a mixture of solutions of potassium dichromate and potassium thiocyanate.<sup>7</sup>

The stable form of potassium dichromate has a density of 2.67,<sup>8</sup> while the monoclinic variety has a density of 2.10.<sup>7</sup> The specific heat of the former, according to Regnault, is 0.1894.<sup>9</sup> It melts at  $897^\circ C.$ , its heat of fusion being 8.77 Calories per gram-molecule.<sup>10</sup>

Potassium dichromate is soluble in water to the extent indicated in the subjoined table :

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100
Grams $K_2Cr_2O_7$ per 100 grams solution <sup>11</sup>	4.43	7.83	11.60	15.40	22.00	27.0	31.30	37.0	42.20	47.0	50.50

<sup>1</sup> Römer, *Ber.*, 1887, 20, Ref. 78.

<sup>2</sup> Jacquelin, *Ann. Chim. Phys.*, 1847, [3], 21, 478, 572.

<sup>3</sup> Schwarz, *Dingl. poly. J.*, 1870, 198, 157; Pontius, *Ber.*, 1883, 16, 813.

<sup>4</sup> For details of the industrial preparation of potassium dichromate, see Ward, *Dingl. poly. J.*, 1865, 177, 239; Carvill, *Zeitsch. Chem.*, 1873, p. 404; Tilghmann, *Ber.*, 1877, 10, 220; Drummond and Donald, *ibid.*, 1878, 11, 1387; Römer, *Zeitsch. Chem.*, 1883, p. 435; Gormann, *ibid.*, 1883, p. 347; Chrystal, *ibid.*, 1883, p. 347; Swindells, *Dingl. poly. J.*, 1885, 122, 239; Rowell, *Ber.*, 1887, 20, 27; Vatel, *Bull. Soc. chim.*, 1891, [3], 5, 371; Segallo, *Ber.*, 1890, 23, 216; Donath, *Dingl. poly. J.*, 1883, 248, 72; Filzinger, *ibid.*, 1879, 231, 93.

<sup>5</sup> Schabus, *Sitzungsber. K. Akad. Wiss. Wien*, 1850, 5, 360; Beor, *Pogg. Annalen*, 1851, 82, 420; Mitscherlich, *ibid.*, 1833, 28, 120; Miers, *Min. Mag.*, 1908, 15, 30; Schubnikoff, *Zeitsch. Kryst. Min.*, 1911, 50, 10.

<sup>6</sup> Dufour, *Compt. rend.*, 1913, 156, 1022; 1914, 159, 200.

<sup>7</sup> Hauser and Herzfeld, *Zeitsch. physikal. Chem.*, 1909, 68, 175.

<sup>8</sup> Wyrouboff, *Bull. Soc. franç. Min.*, 1890, 13, 300; Schroeder (*Ber.*, 1878, 11, 2017) gives a density of 2.751 for the molten salt.

<sup>9</sup> Kopp (*Annalen Suppl.*, 1864, 3, 294) gives 0.186.

<sup>10</sup> Landolt-Börnstein, *Physikalisch-chemische Tabellen* (Berlin), 1912, p. 820.

<sup>11</sup> Interpolated from data given by Kremers, *Pogg. Annalen*, 1854, 92, 499; Michel and Kraft, *Ann. Chim. Phys.*, 1854, [3], 41, 482; Alluard, *Compt. rend.*, 1864, 59, 500; Guthrie, *Phil. Mag.*, 1875, [4], 49, 16; Tilden and Shenstone, *Trans. Chem. Soc.*, 1884, 45, 34; Alluard and Etard, *Ann. Chim. Phys.*, 1894, [7], 2, 550; Koppel and Blumenthal, *Zeitsch. anorg. Chem.*, 1907, 53, 202. See also Sand, *Ber.*, 1906, 39, 2038.

A saturated aqueous solution boils at  $103^{\circ}$  C. The aqueous solution exhibits an acid reaction with litmus paper, has a sharp, metallic taste, and is, of course, poisonous (see p. 45). It absorbs nitric oxide with eventual precipitation of chromium dioxide.<sup>1</sup> Unlike the normal salt, potassium dichromate is strongly adsorbed in solution by animal charcoal.<sup>2</sup>

A concentrated aqueous solution, when mixed with concentrated sulphuric acid and cooled, yields crystals of chromium trioxide (see p. 40);<sup>3</sup> if strongly heated with sulphuric acid, the products are potassium hydrogen sulphate, chromic sulphate, water, and oxygen. At a white heat potassium dichromate itself decomposes, yielding the normal chromate, chromium sesquioxide, and oxygen. It is readily reduced by the usual agents, e.g. by carbon, sulphur, phosphorus,<sup>4</sup> magnesium,<sup>5</sup> hydrogen sulphide, sulphur dioxide (dithionate being formed as well as sulphate), by solid oxalic acid,<sup>6</sup> and by stannous chloride,<sup>7</sup> also electrolytically.<sup>8</sup>

With concentrated hydrochloric acid, or with phosphorus trichloride,<sup>9</sup> potassium chlorochromate is produced (*q.v.*). A compound,  $K_2Cr_2O_7 \cdot HgCl_2$ , has been described.<sup>10</sup> Compounds of dichromates and pyridine have been prepared.<sup>11</sup>

Commercial potassium dichromate is almost chemically pure; it is used in photography, since, in presence of organic substances, it is affected by light.

**Potassium Trichromate**,  $K_2Cr_3O_{10}$ , is obtained by dissolving the dichromate in nitric acid, of density 1.19,<sup>12</sup> or by interaction of potassium dichromate with chromium trioxide or chromic acid,<sup>13</sup> as red monoclinic crystals,<sup>14</sup> of density 1.649, which melt at  $250^{\circ}$  C., and are decomposed by water with formation of dichromate and chromic acid.<sup>15</sup>

**Potassium Tetrachromate**,<sup>17</sup>  $K_2Cr_4O_{13}$ , is prepared similarly to the trichromate (the nitric acid used having density 1.41), and has<sup>18</sup> similar properties. The crystals belong to the monoclinic system.<sup>19</sup>

**Potassium Fluochromate**,  $CrO_2 \cdot OK \cdot F$ , prepared by the action of hydrofluoric acid upon potassium dichromate, has been described.<sup>20</sup>

<sup>1</sup> Vogel, *J. prakt. Chem.*, 1859, 77, 482.

<sup>2</sup> Oryng, *Kolloid. Zeitsch.*, 1913, 13, 9.

<sup>3</sup> Traube, *Annalen*, 1848, 66, 166; Schwarz, *Dingl. poly. J.*, 1877, 186, 31.

<sup>4</sup> Kopp, *Chem. News*, 1864, 9, 278.

<sup>5</sup> Kern, *ibid.*, 1870, 33, 230.

<sup>6</sup> Bothamley, *Trans. Chem. Soc.*, 1887, 51, 159; Werner, *ibid.*, 1888, 53, 602.

<sup>7</sup> Neidle and Witt, *J. Amer. Chem. Soc.*, 1916, 38, 47; Witt, *ibid.*, 1918, 40, 1020.

<sup>8</sup> Wenger and Midhat, *Ann. Chim. anal.*, 1912, 17, 321.

<sup>9</sup> Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 452. For other reactions see Darmstädter, *Ber.*, 1871, 4, 117; de Koninck, *Chem. Zentr.*, 1903, ii, 623.

<sup>10</sup> Darby, *Annalen*, 1848, 65, 204; Hahn, *Arch. Pharm.*, 1850, [2], 99, 147.

<sup>11</sup> Parravano and Pasta, *Zeitsch. anorg. Chem.*, 1907, 57, 240.

<sup>12</sup> Jäger and Krüss, *Ber.*, 1889, 22, 2028; Siowert, *Zeitsch. ges. Naturwiss.*, 1892, 19, 15; Wyruboff, *Bull. Soc. chim.*, 1881, [2], 35, 162; Bothe, *J. prakt. Chem.*, 1849, 46, 184.

<sup>13</sup> Jäger and Krüss, *loc. cit.*; Schreinemakers, *Chem. Zentr.*, 1905, ii, 1067.

<sup>14</sup> Prismatic;  $a : b : c = 0.8437 : 1 : 0.8318$ ;  $\beta = 101^{\circ} 0'$ . See Bothe, *loc. cit.*; Wyruboff, *loc. cit.*

<sup>15</sup> Schroeder, *Annalen*, 1874, 174, 249; Jäger and Krüss, *loc. cit.*; Bothe, *loc. cit.*

<sup>16</sup> See Koppel and Blumenthal, *Zeitsch. anorg. Chem.*, 1907, 53, 228.

<sup>17</sup> Identical with the potassium nitrochromate described by Darmstädter, *Ber.*, 1871, 4,

117. See Wyruboff, *Bull. Soc. chim.*, 1881, [2], 35, 162.

<sup>18</sup> See Schwarz, *Dingl. poly. J.*, 1877, 186, 31; Schreinemakers, *loc. cit.*; Koppel and Blumenthal, *loc. cit.*

<sup>19</sup> Prismatic;  $a : b : c = 0.797 : 1 : 1.110$ ;  $\beta = 91^{\circ} 42'$ . See Wyruboff, *Zeitsch. Kryst. Min.*, 1883, 8, 637.

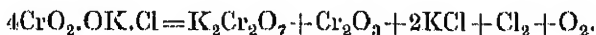
<sup>20</sup> Streng, *Annalen*, 1864, 129, 225; Oudemans, *Rec. Trav. chim.*, 1880, 5, 110.

**Potassium Chlorochromate**,  $\text{CrO}_2\cdot\text{OK}\cdot\text{Cl}$ , may be obtained (a) by warming together a mixture of potassium dichromate and concentrated hydrochloric acid; (b) by the action of chromyl chloride upon a solution of potassium chloride or upon aqueous potassium chromate acidified with acetic acid; <sup>1</sup> (c) by fusion of potassium dichromate with chromic chloride; <sup>2</sup> or (d) by interaction of phosphorus trichloride and potassium dichromate.<sup>3</sup>

Potassium chlorochromate crystallises in the monoclinic system (prismatic):

$$a : b : c = 0.9653 : 1 : 1.0174; \beta = 90^\circ 20',^4$$

isomorphous with the corresponding ammonium salt. The crystals are brownish red in colour, have density 2.407, and are decomposed by fusion: <sup>6</sup>



With sulphuric acid, chromyl chloride is produced.<sup>6</sup>

**Potassium Bromochromate**,  $\text{CrO}_2\cdot\text{OK}\cdot\text{Br}$ , and **potassium iodochromate**,  $\text{CrO}_2\cdot\text{OK}\cdot\text{I}$ , are similar.<sup>7</sup>

**Potassium Chromolodate**,  $\text{KCrO}_3\cdot\text{IO}_3$ , has been prepared.<sup>8</sup> Other compounds are described in other sections of this chapter, and in Vol. II. of this series.

**Rubidium Chromate**,  $\text{Rb}_2\text{CrO}_4$ , crystallises in the bipyramidal class of the rhombic system:

$$a : b : c = 0.5665 : 1 : 0.7490;^9$$

it is obtained by interaction of chromic acid and rubidium carbonate, or fusion of chromium sesquioxide with rubidium nitrate.<sup>10</sup> The double salt,  $\text{Rb}_2\text{Mg}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$ , has been prepared.<sup>11</sup>

**Rubidium Dichromate**,  $\text{Rb}_2\text{Cr}_2\text{O}_7$ , is chiefly of interest on account of its exhibition of dimorphism. The triclinic (pinacoidal)<sup>12</sup> form is probably rather more stable and slightly less soluble than the monoclinic (prismatic)<sup>13</sup> variety.<sup>14</sup>

**Rubidium Trichromate** and **tetrachromate** are decomposed by water.<sup>15</sup>

**Silver Chromate**,  $\text{Ag}_2\text{CrO}_4$ , is obtained as a reddish-brown precipitate on mixing solutions of soluble silver salts with those of chromate or dichromate of potassium; preferably the former.<sup>16</sup> When prepared

<sup>1</sup> Péligot, *Ann. Chim. Phys.*, 1833, 52, 207; Gauthier, *Annalen*, 1858, 106, 240.

<sup>2</sup> Gauthier, *Annalen*, 1858, 108, 68.

<sup>3</sup> Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 449.

<sup>4</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1880, 3, 14.

<sup>5</sup> Oudemans, *Rec. Trav. chim.*, 1880, 5, 116.

<sup>6</sup> For other reactions see Heintze, *J. prakt. Chem.*, 1871, [2], 4, 212; Kletznisky, *Zeitsch. Chem.*, 1866, p. 127; Morgan, *Compt. rend.*, 1878, 86, 1443.

<sup>7</sup> Heintze, *J. prakt. Chem.*, 1871, [2], 4, 225; Guyot, *Compt. rend.*, 1871, 73, 46.

<sup>8</sup> Borg, *Compt. rend.*, 1887, 104, 1514; Blomstrand, *J. prakt. Chem.*, 1889, [2], 40, 330.

<sup>9</sup> Piccard, *J. prakt. Chem.*, 1862, 86, 440; *Bull. Soc. chim.*, 1863, [1], 5, 254; Grandeau, *Ann. Chim. Phys.*, 1863, [3], 67, 227.

<sup>10</sup> For solubility in water see Schreinmakers and Filippo, *Chem. Zentr.*, 1906, i, 1321.

<sup>11</sup> Briggs, *Trans. Chem. Soc.*, 1904, 85, 677; Barker, *ibid.*, 1911, 99, 1327.

<sup>12</sup> Wyruboff states  $a : b : c = 0.5609 : 1 : 0.5690$ ;  $\alpha = 91^\circ 0'$ ;  $\beta = 93^\circ 52'$ ;  $\gamma = 81^\circ 34'$ .

<sup>13</sup> Gossner finds  $a : b : c = 1.0202 : 1 : 1.8081$ ;  $\beta = 93^\circ 28' 30''$ .

<sup>14</sup> Grandeau, *Ann. Chim. Phys.*, 1863, [3], 67, 227; Stortebeker, *Rec. Trav. chim.*, 1907, 26, 240; Wyruboff, *Bull. Soc. chim.*, 1908, [4], 3, 7; Stortebeker, *ibid.*, 1908, [4], 3, 481; Schreinmakers and Filippo, *loc. cit.*; Le Bel, *Compt. rend.*, 1911, 153, 1081. Strömholm (*Zeitsch. anorg. Chem.*, 1912, 75, 277) describes the double salts,  $\text{Rb}_2\text{Cr}_2\text{O}_7\cdot\text{HgCl}_2$  and  $\text{Rb}_2\text{Cr}_2\text{O}_7\cdot\text{Cl}_2\cdot(\text{HgCl}_2)_2\cdot 2\text{H}_2\text{O}$ .

<sup>15</sup> Schreinmakers and Filippo, *loc. cit.*  
<sup>16</sup> Schulerud, *J. prakt. Chem.*, 1870, [2], 19, 36; Bahr, *Jahresber.*, 1853, p. 358; Antenrieth, *Ber.*, 1902, 35, 2057; Margosches, *Zeitsch. anorg. Chem.*, 1904, 41, 68.



by decomposition of the compound  $\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3$  by heat, or by boiling the dichromate with water, it is obtained in a crystalline condition.<sup>1</sup> The latter method of preparation, or concentration of a solution of silver chromate in dilute acetic acid, yields a greenish-black modification.<sup>2</sup> The differences in colour have been connected with differences in density;<sup>3</sup> but, according to Köhler,<sup>4</sup> the colour of pure silver chromate is always greenish black, the red substance, supposed to be a separate modification, being a mixture of silver chromate and solid solutions of the latter with nitrates or other salts present. Pure unfused silver chromate has a density<sup>5</sup> of 5.625 at 25° C.

Silver chromate is almost insoluble in water, glacial acetic acid, and in solutions of potassium chromate, but soluble in those of ammonia, caustic alkalis, nitrates, and in dilute acetic acid.<sup>6</sup> A concentrated solution of ammonium nitrate is a good crystallising medium for silver chromate.<sup>7</sup> With chlorine, above 200° C., silver chloride, chromium trioxide, and oxygen are produced.<sup>8</sup> The solution in ammonia contains the compound  $\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3$ , which forms crystals isomorphous with the corresponding ammoniacal sulphate.<sup>9</sup>

The precipitation of silver chromate under certain conditions has attracted considerable attention since Liesegang<sup>10</sup> observed that when a drop of silver nitrate solution is placed on a gelatin slab impregnated with potassium chromate or dichromate, a precipitate of silver chromate is produced which is not continuous, but which forms in rings separated by clear zones, as diffusion of the silver nitrate through the gel proceeds. These rings are now known as *Liesegang rings*, and the phenomenon as *periodic precipitation*. If the reaction takes place in a test-tube, layers of precipitate are produced.

Various theories have been advanced in explanation.<sup>11</sup> Ostwald suggested that supersaturation took place, followed by precipitation, which cleared the immediate neighbourhood of the reactants, and it was therefore necessary for the silver nitrate to diffuse further before supersaturation was again reached. Hatschek, however, shows that the periodic precipitation takes place in conditions which render supersaturation impossible. Williams and Mackenzie maintain<sup>12</sup> that the silver chromate is precipitated according to the usual rules of the solubility product, and does not behave in any way as a protected colloid but as a crystalloid.<sup>13</sup> More recent work suggests<sup>14</sup> that whenever precipitation takes place, the precipitate first passes through the colloidal

<sup>1</sup> Jäger and Krüss, *Ber.*, 1889, 22, 2028; Autonrieth, *ibid.*, 1902, 35, 2057; Meinecke, *Annalen*, 1891, 261, 341.

<sup>2</sup> Margosches, *Zeitsch. anorg. Chem.*, 1906, 51, 231.

<sup>3</sup> Schröder, *Jahresber.*, 1871, p. 31, states the density of the red variety to be 5.523; of the green variety, 5.536.

<sup>4</sup> Köhler, *Zeitsch. anorg. Chem.*, 1910, 96, 207.

<sup>5</sup> Baxter, Mueller, and Hines, *J. Amer. Chem. Soc.*, 1909, 31, 529.

<sup>6</sup> Meinecke, *loc. cit.*; Margosches, *loc. cit.*

<sup>7</sup> van Eck, *Pharm. Weekblad*, 1916, 53, 1554.

<sup>8</sup> Krutwig, *Ber.*, 1881, 14, 304. See also Freese, *Pogg. Annalen*, 1870, 140, 87; Fischer, *ibid.*, 1826, 8, 488.

<sup>9</sup> Jäger and Krüss, *loc. cit.*; Meinecke, *loc. cit.*; Mitscherlich, *Pogg. Annalen*, 1828, 12, 137. See also Wöhler and Rautenberg, *Annalen*, 1860, 114, 119; Muthmann, *Ber.*, 1887, 20, 984; Szilárd, *Chem. Zentr.*, 1907, i, 223.

<sup>10</sup> Liesegang, *Zeitsch. physikal. Chem.*, 1914, 88, 1; *Chem. Zentr.*, 1914, ii, 1260.

<sup>11</sup> See Hatschek, "Second Report on Colloid Chemistry," *Rep. Brit. Assoc.*, 1919, p. 21.

<sup>12</sup> Williams and Mackenzie, *Trans. Chem. Soc.*, 1920, 117, 844.

<sup>13</sup> See Bradford, *Biochem. J.*, 1920, 14, 29, and M'Guigan, *Science*, 1921, 54, 78, for other explanations.

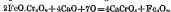
<sup>14</sup> Friend and Vallance, *Trans. Chem. Soc.*, 1922, 121, 406.

condition, coagulation of the molecules into the large precipitated particles being a gradual growth and not an instantaneous transformation. If, therefore, a protective colloid such as gelatin is present, the precipitation will be retarded, since the colloidal particles of silver chromate will tend to adsorb the gelatin, and will therefore remain for a longer time in the colloidal condition. The space between the successive rings is thus determined by the difference between the rates of diffusion and of precipitation in the gel.

Silver Dichromate,  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , is prepared by the addition of silver nitrate to a hot solution of potassium dichromate containing a large excess of nitric acid, and cooling till crystallisation occurs. The salt may readily be recrystallised from nitric acid, traces of which are, however, retained.<sup>1</sup> It crystallises as red-black plates in the triclinic system,<sup>2</sup> and has a density of 4.770.<sup>3</sup> It cannot be dried without decomposition, for it is readily decomposed by water with formation of the neutral chromate and chromic acid.<sup>4</sup>

No trichromate of silver is known, but a *chromiodate*,  $\text{AgCrO}_5\text{IO}_3$ , a *chromicyanide*,  $\text{Ag}_2\text{Cr}(\text{CN})_6$  and a *chromithiocyanate*,  $\text{Ag}_2\text{Cr}(\text{CNS})_6$ , have been described.

Sodium Chromate,  $\text{Na}_2\text{CrO}_4$ , is prepared from *chromite* (p. 7) by fusion with lime, sodium sulphate, and calcium chloride in an oxidising atmosphere, when the following reaction occurs:



The mass is mixed with water and the calculated quantity of sodium hydrogen sulphate, and heated under pressure; after filtration the solution of sodium chromate is fractionally crystallised.<sup>5</sup> If the dichromate is required, the solution of sodium chromate is slightly acidified with sulphuric acid and evaporated until it crystallises.

Sodium chromate may be obtained anhydrous, and in the form of a deca-, hexa-, and tetra-hydrate, according to the conditions of crystallisation. The anhydrous salt,  $\text{Na}_2\text{CrO}_4$ , separates from its solution on evaporation at a temperature above  $62.8^\circ \text{C}$ .<sup>6</sup> It forms yellow crystals in the rhombic system (bipyramidal):

$$a : b : c = 0.4648 : 1 : 0.7901,^7$$

isomorphous with anhydrous sodium sulphate, and of density 2.723.<sup>8</sup> It dissolves in water, forming the above-mentioned hydrates. The following table shows the solubility at various temperatures: <sup>9</sup>

<sup>1</sup> Schulerud, *J. prakt. Chem.*, 1870, [3], 19, 39; Antonicich, *Ber.*, 1902, 35, 2057; Mayor, *ibid.*, 1903, 36, 1749; Varrington, *Analyst*, 1908, 27, 12; Baxter and Jesso, *J. Amer. Chem. Soc.*, 1900, 31, 641.

<sup>2</sup> Pinacoidal;  $a : b : c = 1.5390 : 1 : 1.0546$  (Schubert).

<sup>3</sup> Baxter and Jesso, *loc. cit.*; Schröder, *loc. cit.*, gives  $D = 4.900$ .

<sup>4</sup> Antonicich, *loc. cit.*; Baxter and Jesso, *loc. cit.* See also van Namo and Brewster, *Amer. J. Sci.*, 1910, [4], 29, 263; 1918, [4], 45, 84.

<sup>5</sup> Johnson, *J. prakt. Chem.*, 1864, 62, 201; Kopp, *Annals*, 1842, 42, 30.

<sup>6</sup> Richards and Kolloy, *J. Amer. Chem. Soc.*, 1911, 33, 847. See also Mylius and Funk, *Ber.*, 1900, 33, 3080; Kopp, *loc. cit.*; Reigars, *Zeitsch. physikal. Chem.*, 1891, 8, 47.

<sup>7</sup> Traube, *Zeitsch. Krist. Min.*, 1894, 22, 138; Kopp, *loc. cit.*; Lesomur, *Compt. rend.*, 1880, 103, 1200; Johnson, *loc. cit.*; Berthelot, *Compt. rend.*, 1878, 87, 573.

<sup>8</sup> Clarke, *Amer. J. Sci.*, 1877, [3], 14, 281.

<sup>9</sup> Mylius and Funk, *Wissenschaftl. Abhandl. phys.-tech. Reichsanst.*, 1900, 3, 440; *Ber.*, 1900, 33, 3080; Solkowski, *ibid.*, 1901, 34, 1048; Schminemann, *Chem. Weekblad*, 1904, Nos. 28 and 50; 1905, Nos. 13 and 45; 1906, No. 11; *Zeitsch. physikal. Chem.*, 1900, 55, 71.



lographic elements of  $\text{LiNa}_3(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$  (ditrigonal pyramidal), and  $(\text{NH}_4)\text{NaCrO}_4 \cdot 2\text{H}_2\text{O}$  (rhombic bipyramidal), have also been measured.<sup>1</sup>

Sodium Dichromate,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , may be prepared as

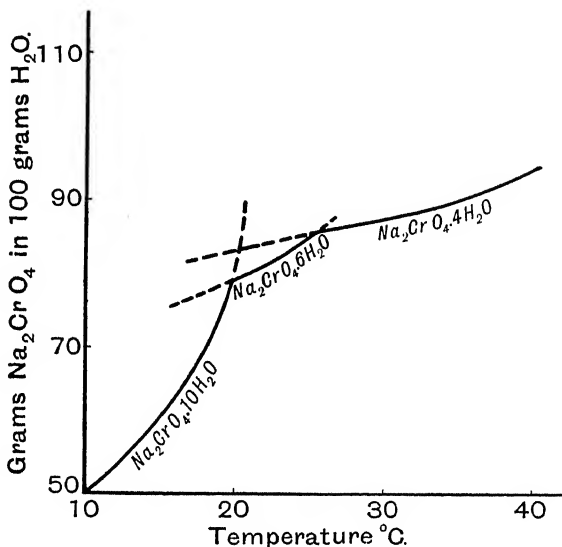


FIG. 1.—Solubility of sodium chromate.

described above, or by methods similar to those described for potassium dichromate on p. 61.<sup>2</sup> It forms hyacinth-red, slender prisms, crystallising in the monoclinic system (prismatic):

$$a : b : c = 0.5698 : 1 : 1.1824; \beta = 94^\circ 55',^3$$

and of density 2.525.<sup>4</sup> It is very soluble in water, the solubility being as follows (see figure 2, p. 68):<sup>5</sup>

Temperature, ° C.	Grams $\text{Na}_2\text{Cr}_2\text{O}_7$ in 100 Grams Solution.	Solid Phase.
0	61.98	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$
18	63.92	"
34.5	67.36	"
52	71.76	"
72	76.9	"
81	79.8	"
93	81.19	$\text{Na}_2\text{Cr}_2\text{O}_7$
98	81.25	"

<sup>1</sup> Traube, *Zeitsch. Kryst. Min.*, 1896, 26, 644; Wyruboff, *ibid.*, 1879, 4, 418.

<sup>2</sup> See also Potter and Higgin, *Ber.*, 1884, 17, Ref. 218; Gormann, *ibid.*, 1885, 18, Ref. 307.

<sup>3</sup> Wyruboff, *Zeitsch. Kryst. Min.*, 1893, 22, 205.

<sup>4</sup> Stanley, *Chem. News*, 1886, 54, 195.

<sup>5</sup> Mylius and Funk, *Ber.*, 1900, 33, 3688. See also Stanley, *loc. cit.*; Siewert, *Zeitsch. ges. Naturwiss.*, 1862, 19, 17; Münzig, *Zeitsch. Kryst. Min.*, 1888, 14, 62.

The density of the saturated solution at 18° C. is 1.745.<sup>1</sup> It melts at 320° C. and decomposes at 400° C.<sup>2</sup>

Sodium dichromate plays an important part in the tanning of leather. There are two methods of chrome tanning in general use—the *two-bath* process and the *one-bath* process. The former was invented by Schulze in 1884, and consists in first treating the skins with a weak bath of sodium dichromate acidified with a mineral acid, when chromic acid is absorbed, colouring the skins bright yellow but producing no tanning effect. The acid is then reduced by transferring the skins to a second bath containing an acidified solution of sodium thiosulphate,

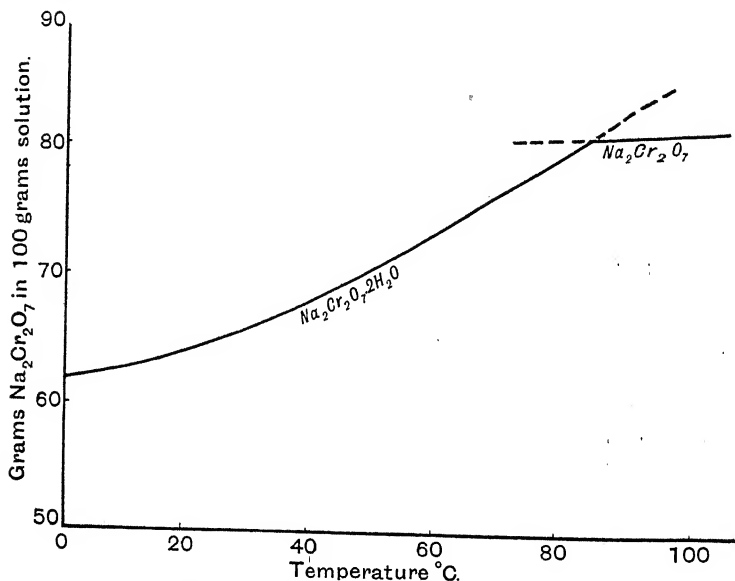
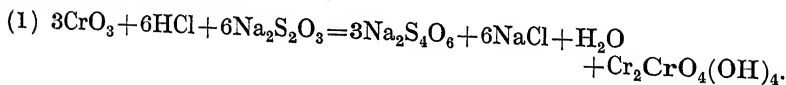


FIG. 2.—Solubility of sodium dichromate.

when basic sulphates are produced which immediately convert the skins into leather, the colour of the latter becoming brown probably owing to the formation of a basic chromium chromate,<sup>3</sup>  $\text{Cr}_2\text{CrO}_4(\text{OH})_4$ , a compound which on heating to about 120° C. yields chromium dioxide (see p. 39). The reactions taking place in the second bath are very complicated; <sup>4</sup> sulphur is deposited on the skins, and sodium tetrathionate is formed in the bath. It has been shown by Stiasny that the tanning is due to basic chromium sulphates even when hydrochloric acid is used in the first bath. The following equations probably show the course of the reactions:



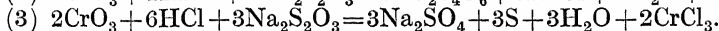
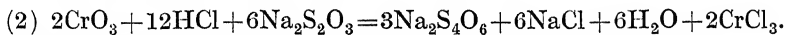
<sup>1</sup> Mylius and Funk, *Ber.*, 1900, 33, 3688.

<sup>2</sup> Stanley, *Chem. News*, 1886, 54, 195.

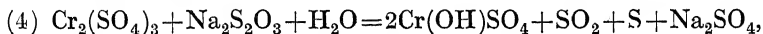
<sup>3</sup> Wood, *Some Scientific Aspects of Tanning*, Institute of Chemistry Lecture, 1920.

<sup>4</sup> Procter, *Principles of Leather Manufacture*, Spon, 1903, p. 206. See also Stiasny and Das, *J. Soc. Chem. Ind.*, 1912, 31, 753, for a careful research on the reaction between sodium thiosulphate and a mixture of potassium dichromate and sulphuric acid.

On further additions of acid the skins brighten in colour, chromic chloride being formed, and sulphur is deposited :



Chromic sulphate is produced by the action of the oxidised thio-sulphate, and the basic salt results after the free hydrochloric acid has been used up, thus :



sulphur being again deposited, chiefly within the skins. The softness of the leathers produced by this process is largely due to this sulphur, which acts as a filling and fibre-isolating substance, but such leathers made in imitation of chamois cannot be used for polishing silver.

In the one-bath process the skins are immersed directly in a solution of chromic sulphate to which a certain amount of alkali has been added. The action depends upon absorption of colloidal basic sulphate.<sup>1</sup>

**Sodium Trichromate**,  $\text{Na}_2\text{Cr}_3\text{O}_{10}$ , is obtained by union of the dichromate with chromic acid as slightly soluble crystals.<sup>2</sup>

**Sodium Tetrachromate**,  $\text{Na}_2\text{Cr}_4\text{O}_{13} \cdot 4\text{H}_2\text{O}$ , is similarly prepared.<sup>3</sup>

**Sodium Chlorochromate**,  $\text{NaClCrO}_3 \cdot 2\text{H}_2\text{O}$ , may be prepared from sodium chromate and chromyl chloride<sup>4</sup> as reddish-yellow crystals, somewhat unstable, especially in solution. A **chromiodate**,  $\text{Na}_2\text{CrO}_3 \cdot \text{IO}_3 \cdot \text{H}_2\text{O}$ , has also been described.<sup>5</sup>

**Stannic Chromate**.—When stannic chloride is added to a solution of potassium chromate a yellow precipitate is formed, while the liquid becomes orange-yellow, free chromic acid being liberated. The precipitate, when dried, becomes brownish yellow and translucent, and on heating changes into violet chromic stannate.<sup>6</sup>

**Stannous Chromate** has been described by Berzelius as a yellow flocculent precipitate resulting on the addition of stannous chloride to an excess of potassium chromate solution. If, however, dilute potassium chromate solution is added in small portions, with constant shaking, to stannous chloride, a greenish-white precipitate is produced which is probably chromic stannate. If the tin solution contains free acid the whole remains dissolved, forming a green solution.

**Strontium Chromate**,  $\text{SrCrO}_4$ , is formed when an alkali chromate is added to solutions of strontium salts. It appears to be dimorphic, since it separates from concentrated solutions as long, slender, highly refracting needles, but from very dilute solutions as thick hexagonal prisms.<sup>7</sup> It is obtained in rhombic scales when strontium chloride is fused with sodium chromate or potassium chromate.<sup>8</sup> It is a yellow powder, of density 3.353,<sup>9</sup> and slightly soluble in water, 1 part being

<sup>1</sup> For accounts of the various methods of chrome tannage, see Procter, *Leather Trades Review*, 1897, p. 390; 1898, p. 400; Cobb Lecture to Society of Arts, 1918; Stiasny, *Collegium*, 1912, p. 293; Wintgen and Löwenthal, *Kolloid. Zeitsch.*, 1924, 34, 289.

<sup>2</sup> Stanley, *loc. cit.*

<sup>3</sup> Mylius and Funk, *Ber.*, 1900, 33, 3686; they also describe a chromate,  $\text{Na}_4\text{CrO}_6 \cdot 13\text{H}_2\text{O}$ .

<sup>4</sup> Prétorius, *Annalen*, 1880, 201, 16.

<sup>5</sup> Berg, *Compt. rend.*, 1887, 104, 1514.

<sup>6</sup> Leykauf, *J. prakt. Chem.*, 1840, 19, 127.

<sup>7</sup> Autenreith, *Ber.*, 1904, 37, 3882.

<sup>8</sup> Bourgeois, *Compt. rend.*, 1879, 88, 382.

<sup>9</sup> Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

dissolved by 831.8 parts of water.<sup>1</sup> It is readily soluble in acids, in solutions of ammonium salts,<sup>2</sup> and in molten sodium nitrate.<sup>3</sup>

*Double salts* of strontium chromate have been obtained<sup>4</sup> by double decomposition with alkali chromate solutions, the latter being concentrated and in excess;  $K_2Sr(CrO_4)_2$  and  $(NH_4)_2Sr(CrO_4)_2$  both yield yellow crystals which are decomposed by water. The additive compound  $(SrCrO_4 \cdot 3HgCl_2)_2 \cdot HCl$  has been described.<sup>5</sup>

**Strontium Dichromate**,  $SrCr_2O_7 \cdot 3H_2O$ , is formed by dissolving the normal chromate in chromic acid solution and allowing to crystallise,<sup>6</sup> or by treating freshly precipitated strontium chromate with solid chromic anhydride.<sup>7</sup> It yields large reddish-brown monoclinic crystals,

$$a : b : c = 0.6023 : 1 : 0.5460 ; \gamma = 87^\circ 28',^8$$

readily soluble in water. On heating, the water of crystallisation is completely expelled at  $110^\circ C$ .

The additive compound  $SrCr_2O_7 \cdot SrCl_2 \cdot 4HgCl_2 \cdot H_2O$  has been obtained.<sup>5</sup>

**Strontium Trichromate**,  $SrCr_3O_{10} \cdot 3H_2O$ , has been prepared<sup>7</sup> as deliquescent garnet-red crystals by treating strontium chromate with a large excess of chromic acid.

**Thallous Chromate**,  $Tl_2CrO_4$ , is precipitated when a solution of a thallous salt is mixed with potassium chromate. It is also produced by adding thallous hydroxide or carbonate to aqueous chromic acid, or by the action of ammonia on the dichromate. Thallous chromate is a yellow crystalline powder, very sparingly soluble in water, 100 grams of which dissolve 0.03 gram of the salt at  $60^\circ C$ ., and 0.2 gram at  $100^\circ C$ .<sup>9</sup>

In hot concentrated potassium hydroxide solution thallous chromate is fairly soluble, and it separates out on cooling in crystals which are apparently isomorphous with potassium chromate.<sup>10</sup> At a dull red heat the chromate melts, and at higher temperatures it loses oxygen.

**Thallic Chromate**,  $Tl_2(CrO_4)_3$ , has not yet been prepared, but potassium thallic chromate,  $K_2CrO_4 \cdot Tl_2(CrO_4)_3 \cdot 4H_2O$ , is known as a yellow crystalline salt decomposed by water.<sup>11</sup>

**Thallous Dichromate**,  $Tl_2Cr_2O_7$ , is precipitated as an orange-red crystalline powder when solutions of a soluble thallous salt and potassium dichromate are mixed,<sup>12</sup> and is also obtained by the action of sulphuric acid on the chromate.<sup>13</sup>

**Thallous Trichromate**,  $Tl_2Cr_3O_{10}$ , a red, crystalline, sparingly soluble salt, is obtained<sup>14</sup> by the action of nitric acid on the dichromate, or of concentrated sulphuric acid on the chromate.

<sup>1</sup> Fresenius, *Zeitsch. anal. Chem.*, 1890, 29, 418. See also Meschezerski, *ibid.*, 1882, 21, 399; Kohlrausch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1897, p. 90.

<sup>2</sup> Fresenius, *loc. cit.*

<sup>3</sup> Guthrie, *Trans. Chem. Soc.*, 1885, 47, 94.

<sup>4</sup> Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185; 1908, 58, 412; Barre, *Compt. rend.*, 1914, 158, 495.

<sup>5</sup> Imbert and Belugon, *Bull. Soc. chim.*, 1897, [3], 17, 471, 473.

<sup>6</sup> Bahr, *J. prakt. Chem.*, 1853, 60, 60; Wyrouboff, *Bull. Soc. franç. Min.*, 1891, 14, 77.

<sup>7</sup> Preis and Rayman, *Ber.*, 1880, 13, 340.

<sup>8</sup> Wyrouboff, *loc. cit.*

<sup>9</sup> Browning and Hutchins, *Amer. J. Sci.*, 1899, [4], 8, 460; *Zeitsch. anorg. Chem.*, 1900, 22, 380.

<sup>10</sup> Lepierre and Lachaud, *Compt. rend.*, 1891, 113, 196.

<sup>11</sup> Hawley, *J. Amer. Chem. Soc.*, 1907, 29, 300.

<sup>12</sup> Crookes, *Chem. News*, 1863, 8, 255.

<sup>13</sup> Willm, *Ann. Chim. Phys.*, 1865, [4], 5, 59.

<sup>14</sup> Crookes, *loc. cit.*; Willm, *loc. cit.*

**Thallous Chlorochromate**,  $\text{CrO}_2(\text{OTl})\text{Cl}$ , obtained from thallous chloride and chromic acid, forms small prismatic crystals decomposed by water.<sup>1</sup>

**Thorium Chromate**,  $\text{Th}(\text{CrO}_4)_3 \cdot 3\text{H}_2\text{O}$ , has been prepared.<sup>2</sup>

**Uranyl Chromate**,  $\text{UO}_2\text{CrO}_4 \cdot 3\text{H}_2\text{O}$ , crystallises in yellow needles on evaporating a saturated solution of uranium trioxide in chromic acid.<sup>3</sup> The crystals effloresce on exposure to air, and become anhydrous, with partial decomposition, at  $200^\circ \text{C}$ . They are readily soluble in water, 1 part of the salt dissolving in 13.3 parts of water; the chromate also dissolves in alcohol, forming a solution which decomposes on exposure to sunlight with separation of a brown precipitate. The addition of potassium chromate to an aqueous solution of uranyl chromate precipitates the *basic salt*,  $\text{UO}_3 \cdot 2\text{UO}_2\text{CrO}_4 \cdot 8\text{H}_2\text{O}$ , potassium dichromate also being formed, thus:



The *basic salt*,  $\text{UO}_3 \cdot \text{UO}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$ , has also been obtained.

*Complex uranyl chromates* may be prepared by treating an alkali uranate with warm concentrated chromic acid solution and evaporating the filtered solution over sulphuric acid. The potassium salt,  $\text{K}_2(\text{UO}_2)_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ , which may also be obtained by evaporating a mixed solution of potassium chromate and uranyl nitrate,<sup>4</sup> forms yellow monosymmetric crystals,

$$a : b : c = 0.7566 : 1 : 1.9714 ; \beta = 72^\circ 38',$$

partially decomposed by water. The ammonium salt,  $(\text{NH}_4)_2(\text{UO}_2)_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ , is isomorphous with the potassium salt,

$$a : b : c = 0.8016 : 1 : 1.0196 ; \beta = 72^\circ 31'.$$

The sodium salt,  $\text{Na}_2(\text{UO}_2)_2(\text{CrO}_4)_3 \cdot 10\text{H}_2\text{O}$ , separates in yellow warty crystals, which readily dissolve in water.

A pyridine compound,  $(\text{UO}_3)_2(\text{CrO}_3)_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ , has been obtained in the form of lustrous orange-coloured crystals.<sup>5</sup>

**Zinc Chromate**,  $\text{ZnCrO}_4$ , may be obtained by heating together potassium dichromate solution and excess of zinc hydroxide in a sealed tube at  $220^\circ \text{C}$ .,<sup>6</sup> or by heating zinc carbonate with chromic acid in aqueous solution.<sup>5</sup> It forms small lemon-yellow crystals. According to Gröger,<sup>7</sup> who has investigated the conditions of equilibrium in the system  $\text{ZnO} - \text{CrO}_3 - \text{H}_2\text{O}$ , the *monohydrate*,  $\text{ZnCrO}_4 \cdot \text{H}_2\text{O}$ , may be crystallised from solutions containing more than 9.7 molecules of  $\text{CrO}_3$  (and 4.78 molecules of  $\text{ZnO}$ ). It yields microscopic lemon-yellow prisms, which may be heated to  $125^\circ \text{C}$ . without loss of water.

Zinc chromate is decomposed by water, forming basic chromates,<sup>8</sup>

<sup>1</sup> Lepierre and Lachaud, *loc. cit.*

<sup>2</sup> Britton, *Trans. Chem. Soc.*, 1923, 123, 1429. See also Palmer, *Amer. Chem. J.*, 1895, 17, 374; Haber, *Sitzungsber. K. Akad. Wiss. Wien*, 1897, [iib], 106, 690; *Monatsh.*, 1897, 18, 687.

<sup>3</sup> Orloff, *Chem. Zeit.*, 1907, 31, 375. Formánek (*Annalen*, 1890, 257, 102), using uranyl hydroxide, obtained similar crystals, to which he gave the formula  $\text{UO}_2\text{CrO}_4 \cdot 11\text{H}_2\text{O}$ .

<sup>4</sup> Formánek, *loc. cit.*

<sup>5</sup> Briggs, *Zeitsch. anorg. Chem.*, 1907, 56, 246.

<sup>6</sup> Schulze, *ibid.*, 1895, 10, 148.

<sup>7</sup> Gröger, *ibid.*, 1911, 70, 135.

<sup>8</sup> Gröger, *loc. cit.* The identity of these basic chromates is questioned by Britton (*Trans. Chem. Soc.*, 1926, p. 134).



the following having been separated:  $4\text{ZnO} \cdot \text{CrO}_3 \cdot 3\text{H}_2\text{O}$ ;  $3\text{ZnO} \cdot \text{CrO}_3 \cdot 2\text{H}_2\text{O}$ ;  $4\text{ZnO} \cdot 2\text{CrO}_3 \cdot 3\text{H}_2\text{O}$ ;  $3\text{ZnO} \cdot 2\text{CrO}_3 \cdot \text{H}_2\text{O}$ —this being the order of their existence. Basic salts, for example,  $4\text{ZnO} \cdot \text{CrO}_3 \cdot \text{H}_2\text{O}$ , are also formed by precipitation of zinc salts with sodium chromate, or by decomposition of the double salts with water. These compounds are used as pigments under the names of zinc yellow, zinc chrome, and citron yellow, and possess the advantage over lead chromes of not being discoloured by hydrogen sulphide or by contact with sulphide pigments. In "body" they are not equal to the lead chromes, however, and are therefore not largely used as separate pigments. Mixed with Prussian blue they yield the various zinc greens.<sup>1</sup>

*Double chromates* of zinc and the alkali metals have been described. The potassium compound  $\text{K}_2\text{Zn}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$  is obtained in the form of light yellow prismatic crystals when an excess of a concentrated potassium chromate solution is added to a solution of a zinc salt.<sup>2</sup> The compounds  $\text{K}_2\text{O} \cdot 4\text{ZnO} \cdot 4\text{CrO}_3 \cdot 3\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{O} \cdot 2\text{ZnO} \cdot 2\text{CrO}_3 \cdot \text{H}_2\text{O}$  have been formulated, but their individuality has not been definitely established.<sup>3</sup>

The following compounds containing ammonia have been obtained<sup>4</sup> by the action of excess of ammonium chromate on salts of zinc, or by precipitating ammoniacal solutions of zinc chromate by means of alcohol:  $\text{ZnCrO}_4 \cdot 4\text{NH}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{ZnCrO}_4 \cdot 4\text{NH}_3 \cdot 5\text{H}_2\text{O}$ ;  $\text{ZnCrO}_4 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$ ;  $4\text{ZnCrO}_4 \cdot 2(\text{NH}_4)_2\text{CrO}_4 \cdot 3\text{NH}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{ZnCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 2\text{NH}_3$ ;  $2\text{ZnO} \cdot 3\text{CrO}_3 \cdot 10\text{NH}_3 \cdot 10\text{H}_2\text{O}$ ;  $2(\text{ZnCrO}_4 \cdot 4\text{NH}_3) \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 9\text{H}_2\text{O}$ .

*Zinc Dichromate*,  $\text{ZnCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , is obtained<sup>5</sup> by evaporation of a solution of zinc carbonate in cold aqueous chromic acid. It yields, when pure, orange-red crystals, but the colour is usually dark red. The crystals are hygroscopic and readily dissolve in water, by which the dichromate is decomposed on boiling.

The *double salt*,  $\text{ZnCr}_2\text{O}_7 \cdot 2\text{Hg}(\text{CN})_2 \cdot 7\text{H}_2\text{O}$ , has been obtained.<sup>6</sup>

*Zinc Trichromate*,  $\text{ZnCr}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ , is prepared<sup>7</sup> by treating a solution of the dichromate with excess of chromic acid. It forms deliquescent, reddish-brown prismatic crystals.

*Chromates of the Rare Earth Metals*.—A series of isomorphous yellow chromates, sparingly soluble in water, and of general formula  $\text{R}_2 \cdot (\text{CrO}_4)_3 \cdot 8\text{H}_2\text{O}$ , where  $\text{R}$ =Lanthanum, Praseodymium, Neodymium, or Samarium, has been prepared.<sup>8</sup>

#### PERCHROMIC ACID AND PERCHROMATES.

When hydrogen peroxide is added to an acidified aqueous solution of a chromate, oxidation occurs and a deep indigo-blue colour results.<sup>9</sup> The reaction is extremely delicate, and may be used as a test for either

<sup>1</sup> For the application of these compounds in the pigment industry, see Bock, *Kolloid. Zeitsch.*, 1917, 20, 145.

<sup>2</sup> Gröger, *ibid.*, 1907, 54, 185.

<sup>3</sup> Gröger, *Monatsh.*, 1904, 25, 520; Bock, *loc. cit.*

<sup>4</sup> Malaguti and Sarzeau, *Ann. Chim. Phys.*, 1843, [3], 9, 431; Bieler, *Annalen*, 1869, 151, 223; Briggs, *J. Chem. Soc.*, 1904, 85, 672; Gröger, *Zeitsch. anorg. Chem.*, 1908, 58, 412.

<sup>5</sup> Schulze, *Zeitsch. anorg. Chem.*, 1895, 10, 148; Gröger, *ibid.*, 1910, 66, 7.

<sup>6</sup> Krüss and Unger, *ibid.*, 1895, 8, 45.

<sup>7</sup> Britton, *Trans. Chem. Soc.*, 1924, 125, 1875. The system  $\text{La}_2(\text{CrO}_4)_3 - \text{K}_2\text{CrO}_4 - \text{H}_2\text{O}$

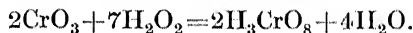
has been investigated by Carobbi (*Atti R. Accad. Lincei*, 1924, [5], 33, ii, 416).

<sup>9</sup> Barreswill, *Ann. Chim. Phys.*, 1847, [3], 20, 364. The reaction is sometimes referred to as Barreswill's reaction.

reactant (see p. 105). The blue product is very unstable, rapidly losing oxygen and yielding a chromium salt, but it remains undecomposed for a longer time if dissolved in ether, amyl alcohol, or ethyl acetate. The isolation of definite "perchromic" compounds from such solutions has been attended with great difficulty.<sup>1</sup> By evaporation of the ethereal solution at  $-20^{\circ}\text{C}$ ., Moissan obtained a blue oily substance, which he formulated as  $\text{CrO}_3 \cdot \text{H}_2\text{O}_2$ , and salts of composition  $\text{BaCrO}_5$  and  $\text{Na}_6\text{Cr}_2\text{O}_5 \cdot 28\text{H}_2\text{O}$ , prepared by suitable neutralisation of the blue solution, have been described.<sup>2</sup> Definite perchromates, however, were not isolated until 1897.<sup>3</sup> A free perchromic acid, of composition  $\text{H}_3\text{CrO}_8 \cdot 2\text{H}_2\text{O}$ , has now been prepared, and four<sup>4</sup> types of derivatives have been shown, with reasonable certainty, to exist:

- (1) Alkali perchromates of the type  $\text{R}'_3\text{CrO}_8$ , reddish brown in colour;
- (2) Alkali salts of the type  $\text{R}'\text{H}_2\text{CrO}_7$  or  $\text{R}'\text{CrO}_5 \cdot \text{H}_2\text{O}_2$ , blue in colour;
- (3) Derivatives of chromium tetroxide; for example, chromium tetroxide triamine,  $\text{CrO}_4 \cdot 3\text{NH}_3$ ;
- (4) Perchromates of organic bases of the type  $\text{HCrO}_5 \cdot \text{X}$ .

**Perchromic Acid,  $\text{H}_3\text{CrO}_8 \cdot 2\text{H}_2\text{O}$** , may be prepared<sup>5</sup> by the interaction at  $-30^{\circ}\text{C}$ . of chromium trioxide and 97 per cent. hydrogen peroxide in methyl-ether solution. The reaction proceeds according to the equation



The blue ethereal solution is poured off from excess of either reagent, dried with phosphorus pentoxide and evaporated *in vacuo* at  $-30^{\circ}\text{C}$ . The pure acid remains as a dark blue crystalline mass, which decomposes at a few degrees above  $-30^{\circ}\text{C}$ .

The **red perchromates**, belonging to the first type, are formed by the action of hydrogen peroxide on well-cooled *alkaline*, aqueous solutions of chromates. Red *ammonium* perchromate,  $(\text{NH}_4)_3\text{CrO}_8$ , for example, may be prepared as a reddish-brown, well-crystallised salt by the interaction at a low temperature of 30 per cent. hydrogen peroxide and an ammoniacal solution of ammonium chromate.<sup>6</sup> The correspond-

<sup>1</sup> See Schönbein, *J. prakt. Chem.*, 1859, 79, 69; 1860, 80, 257; Aschoff, *ibid.*, 1860, 81, 401; Werther, *ibid.*, 1861, 83, 195; Storer, *ibid.*, 1860, 80, 44; *Proc. Amer. Acad. Arts Sci.*, iv., 338; Brodie, *Phil. Trans.*, 1850, 140, 759; *Trans. Chem. Soc.*, 1863, 16, 326; Fairley, *Chem. News*, 1876, 33, 238; Moissan, *Compt. rend.*, 1883, 97, 96; Martinon, *Bull. Soc. chim.*, 1886, 45, 862; Carnot, *Compt. rend.*, 1888, 107, 948, 997, 1150; Berthelot, *ibid.*, 1889, 108, 24, 157, 447; Baumann, *Zeitsch. angew. Chem.*, 1891, 4, 135; Marchlewski, *ibid.*, 1891, 4, 392; Griggi, *L'Orosi*, 1892, p. 295; Grosvenor, *J. Amer. Chem. Soc.*, 1895, 17, 41; Bach, *Ber.*, 1902, 35, 872; Patten, *Amer. Chem. J.*, 1903, 29, 385; Karslake, *J. Amer. Chem. Soc.*, 1909, 31, 250. See also Price, *Peracids and their Salts*, Longmans, 1912, p. 92.

<sup>2</sup> Péchard, *Compt. rend.*, 1891, 113, 39; Häussermann, *J. prakt. Chem.*, 1893, [2], 48, 70. Cf. Wiede, *Ber.*, 1897, 30, 2179.

<sup>3</sup> See Wiede, *Ber.*, 1897, 30, 2178; 1898, 31, 516, 3139; 1899, 32, 378.

<sup>4</sup> Byers and Reid (*Amer. Chem. J.*, 1904, 32, 503) describe a compound  $\text{K}_2\text{Cr}_2\text{O}_8$  analogous to the persulphates. That such a compound should exist appears within the limits of probability, but so far no confirmation of its existence has been forthcoming.

<sup>5</sup> Riesenfeld and Mau, *Ber.*, 1914, 47, 548.

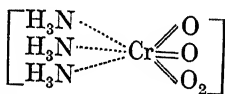
<sup>6</sup> Riesenfeld, Wohlers, and Kutsche, *ibid.*, 1905, 38, 3380. See also Riesenfeld and others, *ibid.*, 1905, 38, 1885, 3578, 4068; 1908, 41, 2826, 3536, 3941; 1911, 44, 147; *Ber. Naturforsch. ges. Freiburg*, 1906, 17, 1. Cf. Hofmann and Hiendlmaier, *Ber.*, 1904, 37, 1663, 3405.

ing *sodium* salt forms reddish-yellow, doubly refractive, glistening plates, while the *potassium* salt is darker in colour than the ammonium salt, which it resembles in other respects. These salts are readily reduced, even by moderately dilute alcohol, at ordinary temperatures. They are unstable in the dry state, and on heating sometimes evolve oxygen explosively.

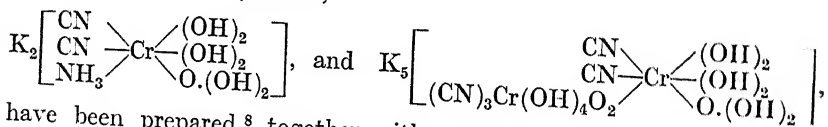
**Blue perchromates**, which are referred to the second type,  $R'H_2CrO_7$  or  $R'CrO_5 \cdot H_2O_2$ , are formed by the interaction at a low temperature of 30 per cent. hydrogen peroxide with *acid* solutions of chromates; <sup>1</sup> a modified method of preparation consists in the neutralisation of a cooled blue ethereal solution of perchromic acid by an alcoholic solution of the alkali.<sup>2</sup> Similar to the red salts, the crystalline blue perchromates are unstable; in the moist condition they are even more so than the red variety, but both forms may best be preserved by keeping in an atmosphere saturated with aqueous vapour.<sup>3</sup>

**Chromium Tetroxide Triamine**,  $CrO_4 \cdot 3NH_3$ , may be obtained by several methods,<sup>4</sup> one consisting of heating the red ammonium perchromate with 10 per cent. ammonia at 40° C., when crystals are obtained of which the form appears to depend upon the concentration of ammonia.<sup>5</sup> The mother-liquor, from which red ammonium perchromate separates in the preparation of that salt, also yields chromium tetroxide triamine upon heating and cooling. It separates in long brown needles or rhombic plates, the density of which at 15.8° C. is 1.964.

The compound is soluble in ammonia and in water (though with partial decomposition), and explodes on moderately heating.<sup>6</sup> With alkalis it yields chromates; with acids, chromic salts and hydrogen peroxide are formed. In both cases gaseous oxygen is evolved. Its properties being those of an ammine and not of an ammonium salt, it may be formulated thus: <sup>7</sup>



The compounds  $CrO_4 \cdot 3KCN$ ,



have been prepared,<sup>8</sup> together with analogous ethylenediamine and hexamethylenetetramine compounds.<sup>9</sup>

**Compounds of perchromic acid with certain organic bases**, the formulæ of which are of the type  $HCrO_5 \cdot X$ , are also blue or violet in colour. The triethylamine, aniline, pyridine, piperidine, and quino-line salts have been prepared. The pyridine salt, for example, is pre-

<sup>1</sup> Riesenfeld and others, *loc. cit.*

<sup>2</sup> Riesenfeld, Wohlers, and Kutsch, *loc. cit.*

<sup>3</sup> Wiede, *loc. cit.*; Riesenfeld and others, *loc. cit.*; Werner, *Ber.*, 1908, 41, 2826.

<sup>4</sup> Wiede, *loc. cit.*; Riesenfeld and others, *loc. cit.*; Werner, *Ber.*, 1908, 41, 3536.

<sup>5</sup> Riesenfeld, Kutsch, and Ohl, *Ber.*, 1905, 38, 3059.

<sup>6</sup> Hofmann and Hiendlmaier, *ibid.*, 1905, 38, 3059.

<sup>7</sup> Wiede, *loc. cit.* See Werner, *loc. cit.*; Riesenfeld, *loc. cit.*

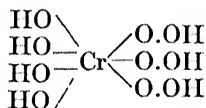
<sup>8</sup> Hofmann and Hiendlmaier, *Ber.*, 1906, 39, 3181.

<sup>9</sup> Wiede, *loc. cit.*

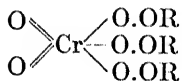
pared<sup>1</sup> as a blue crystalline compound by the addition of hydrogen peroxide to an aqueous solution of chromic acid containing excess of pyridine, or by the addition of excess of pyridine to either the red or the blue ammonium perchromate. It is only slightly soluble in water, and is stable only when in a dry condition. It is decomposed with detonation by moderate heating, or by addition to concentrated sulphuric acid.

A tetramethyl-ammonium derivative,  $N(CH_3)_4CrO_5$ , is also known.<sup>2</sup>

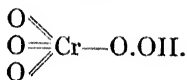
*Constitution of Perchromic Acid and the Perchromates.*—The properties of the blue perchromic acid,  $H_3CrO_8 \cdot 2H_2O$ , indicate that the water is present as water of constitution, and the chromium appears to function as a heptavalent element, a condition which would not be anticipated by consideration of its position in the Periodic classification of the elements. The following formula has therefore been suggested :



and the red perchromates may be regarded as anhydro-salts of the blue perchromic acid, thus :



whereas the blue perchromates and compounds of the type  $HCrO_5 \cdot X$  may be regarded as derivatives of an unknown acid of composition



These formulæ are based on the proportions of peroxidic oxygen which appear to be present in the compounds. The accurate determination of such oxygen, however, is attended with difficulty, and it must not be assumed that the question of the constitution of the perchromates has been finally settled.<sup>3</sup>

#### CHROMIUM AND SULPHUR.

Three sulphides of chromium, possessing respectively the formulæ  $CrS$ ,  $Cr_3S_4$ , and  $Cr_2S_3$ , are known.

**Chromous Sulphide**,  $CrS$ , may be obtained by heating chromous chloride in hydrogen sulphide at  $440^\circ C.$ ,<sup>4</sup> or metallic chromium may be used at very much higher temperatures ;<sup>5</sup> it is also obtained by heating chromic sulphide,  $Cr_2S_3$ , in hydrogen,<sup>6</sup> or by interaction of

<sup>1</sup> Riesenfeld and others, *Ber.*, 1905, 38, 3380.

<sup>2</sup> Wiede, *loc. cit.* ; Riesenfeld, *Ber.*, 1905, 38, 3380 ; 1908, 41, 3941.

<sup>3</sup> See Riesenfeld, *Ber.*, 1911, 44, 147 ; *Zeitsch. anorg. Chem.*, 1912, 74, 48 ; Spitalsky, *ibid.*, 1907, 53, 184 ; 54, 265 ; 56, 72 ; 1910, 69, 179 ; *Ber.*, 1910, 43, 3187.

<sup>4</sup> Moissan, *Compt. rend.*, 1880, 90, 817

<sup>5</sup> Mourlot, *ibid.*, 1895, 121, 943.

<sup>6</sup> Moissan, *loc. cit.* ; Wedekind and Horst, *Ber.*, 1915, 48, 105. Traube, *Annalen*, 1848, 66, 98, states that the pyrophoric residue obtained on heating to redness chromic sulphate in hydrogen consists of a mixture of chromous sulphide and chromium sesquioxide. Cf. Kopp, *Compt. rend.*, 1844, 18, 1156.

aqueous solutions of a chromous salt and alkali sulphide. It is a black powder, or glistening prisms, of density 3.909 at 14° C.<sup>2</sup> It is obtained in a crystalline form by treating with nitric acid the cubical crystals of the double sulphide,  $\text{Al}_2\text{S}_3 \cdot \text{CrS}$ , which result on heating a mixture of aluminium and chromium in hydrogen sulphide, and treating the mass with water.<sup>3</sup> Chromous sulphide is oxidised on heating in air, but is scarcely attacked by acids.

**Chromium Tetrasulphide**,  $\text{Cr}_3\text{S}_4$ , is prepared by heating a mixture of chromium sesquioxide and sulphur in hydrogen. It is a greyish-black powder, insoluble in water and sulphuric acid, but easily soluble in nitric acid.<sup>4</sup>

**Chromic Sulphide**,  $\text{Cr}_2\text{S}_3$ , is formed when dry hydrogen sulphide is passed over chromium sesquioxide at 440° C. or over heated chromium sesquichloride, excess of sulphur being removed with carbon disulphide.<sup>5</sup> It may also be obtained by the action of carbon disulphide upon heated chromic oxide,  $\text{Cr}_2\text{O}_3$ , or potassium dichromate.<sup>6</sup> Another method consists<sup>7</sup> in heating the sesquioxide, or metallic chromium, in carbon disulphide vapour.

Chromic sulphide is a brownish-black, lustrous amorphous powder, of density 3.538 at 14° C.<sup>8</sup> When heated in air it gives sulphur dioxide and chromium sesquioxide, while in hydrogen it yields chromous sulphide. It is attacked and oxidised by nitric acid, aqua regia, and fused potassium nitrate. Compounds of chromic sulphide with sulphides of other metals have been described.<sup>9</sup> Regarding chromic sulphide as the thioanhydride of thiochromous acid,  $\text{H}_2\text{Cr}_2\text{S}_4$ , these compounds may be described as **thiochromites**.

**Sodium Thiochromite**,  $\text{Na}_2\text{Cr}_2\text{S}_4$ , is obtained when 1 part of potassium chromate is fused with 30 parts of sulphur and 15 parts each of sodium carbonate and potassium carbonate. The small brownish-grey crystals have a density of 2.55 at 15° C.

**Potassium Thiodichromite**,  $\text{K}_2\text{Cr}_4\text{S}_7$ , is obtained when 1 part of potassium chromate is fused with 24 parts of potassium carbonate and 24 parts of sulphur to a bright red heat, the mass cooled slowly, and then being thoroughly but rapidly washed with cold water. The crystals, which are reddish or bluish-grey hexagonal plates, of density 2.77 at 15° C., are stable in air.

By the action of hydrochloric acid on these substances in absence of air, **thiochromous acid**,  $\text{H}_2\text{Cr}_2\text{S}_4$ , and **thiodichromous acid**,  $\text{H}_2\text{Cr}_4\text{S}_7$ , are respectively obtained.<sup>10</sup>

Thiochromites of the heavy metals may be obtained by boiling

<sup>1</sup> Mourlot, *Compt. rend.*, 1898, 127, 182; *Ann. Chim. Phys.*, 1899, [7], 17, 529; Moissan, *Compt. rend.*, 1880, 90, 817.

<sup>2</sup> Wedekind and Horst, *Ber.*, 1915, 48, 105.

<sup>3</sup> Houdard, *Compt. rend.*, 1907, 144, 1114.

<sup>4</sup> Gröger, *Ber.*, 1881, 14, 512; *Monatsh.*, 1880, 1, 242.

<sup>5</sup> Moissan, *Compt. rend.*, 1880, 90, 817; *ibid.*, 1881, 92, 1051; Harten, *Annalen*, 1841, 37, 349; Wedekind and Horst, *loc. cit.* See also Traube, *Annalen*, 1848, 66, 98.

<sup>6</sup> Fellenberg, *Pogg. Annalen*, 1840, 50, 77; Schafarik, *J. prakt. Chem.*, 1863, 90, 9; Müller, *Pogg. Annalen*, 1866, 127, 404.

<sup>7</sup> Rose, Gautier, and Hallopeau, *Compt. rend.*, 1889, 108, 806, 1111.

<sup>8</sup> Wedekind and Horst, *loc. cit.* See also Schafarik, *loc. cit.*

<sup>9</sup> Gröger, *Monatsh.*, 1880, 2, 242; Berzelius, *Pogg. Annalen*, 1826, 8, 422; Phipseon, *Chem. News*, 1861, 4, 125; Bender, *Ber.*, 1887, 20, 726; Brückner, *Monatsh.*, 1906, 27, 199; Houdard, *Compt. rend.*, 1907, 144, 1114.

<sup>10</sup> Schneider, *J. prakt. Chem.*, 1897, [2], 56, 401; 1898, 57, 208.

solutions of their salts with sodium thiochromite. Thus compounds of the type  $M'Cr_2S_4$ , where  $M' = Cu, Ag_2, Zn, Cd, Sn, Pb, Mn, Fe, Co, Ni$ , have been prepared.<sup>1</sup> They are greyish-black, insoluble substances, unacted upon by hydrochloric acid, but readily decomposed by nitric acid or aqua regia.

**Chromic Sulphite.**<sup>2</sup>—The normal salt is not known. On boiling the green solution obtained by dissolving chromic hydroxide in aqueous sulphurous acid,<sup>3</sup> or on the addition of alcohol, a green basic sulphite, of composition  $Cr_2(SO_3)_3 \cdot 2Cr(OH)_3 \cdot 13H_2O$ , separates. Other basic sulphites have been described,<sup>5</sup> as also have **chromic dithionate**,<sup>6</sup>  $Cr_2(S_2O_6)_3 \cdot 18H_2O$ , and the compound  $3Cr_2O_3 \cdot 4S_2O_5 \cdot 24H_2O$ .

**Chromous Sulphate**,  $CrSO_4 \cdot 7H_2O$ , is produced by dissolving chromous acetate in dilute sulphuric acid, or by interaction of chromium and sulphuric acid.<sup>7</sup> It forms blue crystals, isomorphous with those of  $FeSO_4 \cdot 7H_2O$ , and is soluble in water, though not in alcohol. It is readily oxidised by the oxygen of the air. Moissan describes a hydrate,  $CrSO_4 \cdot H_2O$ , as a white powder, which with water regenerates the heptahydrate.<sup>8</sup>

Several double sulphates of divalent chromium exist: *sodium chromous sulphate*,  $Na_2SO_4 \cdot CrSO_4 \cdot 4H_2O$ , is prepared<sup>9</sup> by the action of chromous acetate upon a mixture of sodium sulphate and sulphuric acid. The *potassium salt*,  $K_2SO_4 \cdot CrSO_4 \cdot 6H_2O$ , is obtained<sup>10</sup> by alcoholic precipitation of a mixture of chromous chloride and potassium sulphate in solution in absence of air. An *ammonium salt*,  $(NH_4)_2SO_4 \cdot CrSO_4 \cdot 6H_2O$ , has also been prepared.<sup>11</sup>

**Chromic Sulphate**,<sup>12</sup>  $Cr_2(SO_4)_3$ .—The *anhydrous salt* is prepared by dehydration of a hydrate in air at  $400^\circ C$ ,<sup>13</sup> or in a current of carbon dioxide at temperatures rather above  $280^\circ C$ .<sup>14</sup> It forms bluish-red crystals, of density 3.012,<sup>15</sup> insoluble in water and acids.

**Violet Chromium Sulphates**.—Chromic sulphate can be obtained in aqueous solution by dissolving chromic hydroxide (dried at  $100^\circ C$ .) in the calculated quantity of warm sulphuric acid, allowing the green solution to stand for a week, when it becomes blue in colour (although

<sup>1</sup> Gröger, *Monatsh.*, 1881, 2, 266; *Sitzungsber. K. Akad. Wiss. Wien*, 1881, 83, 749; Schneider, *loc. cit.*

<sup>2</sup> Muspratt, *Annalen*, 1844, 50, 259; Manzoni, *Gazzetta*, 1884, 14, 360.

<sup>3</sup> Berthier, *Ann. Chim. Phys.*, 1832, [2], 50, 370; Recoura, *Bull. Soc. chim.*, 1898, [3], 19, 160.

<sup>4</sup> Danson, *Quart. J. Chem. Soc.*, 1848, 2, 205; Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 217.

<sup>5</sup> Seubert and Elton, *Zeitsch. anorg. Chem.*, 1893, 4, 76.

<sup>6</sup> Krüss, *Annalen*, 1888, 246, 189.

<sup>7</sup> Moissan, *Bull. Soc. chim.*, 1882, [2], 37, 296; Péligot, *Ann. Chim. Phys.*, 1844, [3], 12, 548.

<sup>8</sup> See also Bommelen, *Rec. Trav. chim.*, 1887, 6, 202; Whitney, *Zeitsch. physikal. Chem.*, 1896, 20, 44.

<sup>9</sup> Laurent, *Thèse Pharmacie* (Paris), 1901.

<sup>10</sup> Péligot, *Ann. Chim. Phys.*, 1844, [3], 12, 546.

<sup>11</sup> Laurent, *Compt. rend.*, 1900, 131, 111.

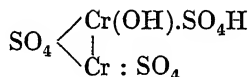
<sup>12</sup> For a general discussion of the constitution of the chromic sulphates, and for a comprehensive survey of the field of inquiry, see Urbain and Sénéchal, *Introduction à la Chimie des Complexes* (Paris), 1913, p. 361. For magneto-chemical data of the violet and green chromic sulphates, see Cabrera and Marquina, *Anal. Fis. Quim.*, 1917, 15, 199.

<sup>13</sup> Sénéchal, *Compt. rend.*, 1914, 159, 243.

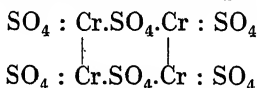
<sup>14</sup> Schrötter, *Pogg. Annalen*, 1841, 53, 520; Siewert, *Annalen*, 1863, 126, 101.

<sup>15</sup> Nilson and Pettersson, *Ber.*, 1880, 13, 1459. Cf. Favre and Valson, *Compt. rend.*, 1873, 77, 579.

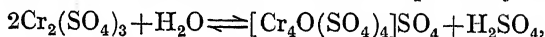
reddish by transmitted light) and deposits violet crystals, or by allowing to crystallise a mixture of sulphuric acid and a solution of chrome alum.<sup>1</sup> These regular octahedral crystals, which have density 1.867,<sup>2</sup> are easily soluble in water to a blue solution, but the substance may be reprecipitated by alcohol.<sup>3</sup> Two violet hydrates, viz.  $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$  and  $\text{Cr}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ , are definitely known, though the existence of others containing  $12\text{H}_2\text{O}$ ,  $14\text{H}_2\text{O}$ , and  $16\text{H}_2\text{O}$  respectively has been suggested.<sup>4</sup> Colson<sup>5</sup> observed that a green solution of chromic sulphate on exposure to sunlight, in becoming turquoise blue in colour, increased in density; it was assumed to contain the compound



*Green Chromium Sulphates.*—When the solid violet salt is heated above  $90^\circ \text{C}$ . a green amorphous mass is obtained. Contrary to the opinion of Wyruboff,<sup>6</sup> Colson<sup>7</sup> considers that this substance may be regarded as a condensed sulphate; for example,



A green amorphous precipitate is also obtained when a violet aqueous solution is evaporated at temperatures between  $70^\circ$  and  $100^\circ \text{C}$ . It has been observed<sup>8</sup> that a violet solution becomes green on the addition of alkalies or alkali carbonates, whereas potassium nitrite and thiocyanate produce the contrary effect. This change from violet to green is accompanied by an increase in acidity, and is apparently due to hydrolysis, together with change of structure—probably as follows :<sup>9</sup>



a *pentasulphate* being formed.

This conclusion is based upon considerations of cryoscopic and conductivity measurements, a study of absorption spectra, and upon observations regarding precipitation with barium chloride in aqueous solution. It is found that precipitation often takes place only to a fraction of the theoretical extent; in fact Colson<sup>10</sup> divides normal

<sup>1</sup> Higley, *J. Amer. Chem. Soc.*, 1904, 26, 613.

<sup>2</sup> Favre and Valson, *Compt. rend.*, 1873, 77, 803. Cf. Schrötter, *Pogg. Annalen*, 1841, 53, 513.

<sup>3</sup> Schrötter, *loc. cit.* See also Löwel, *J. Pharm.*, 1845, [3], 7, 321; Baubigny, *Compt. rend.*, 1884, 98, 100. Traube, *Annalen*, 1848, 66, 168, and Étard, *Compt. rend.*, 1877, 84, 1089, obtained the hydrate by reduction of chromic acid by means of alcohol or ether.

<sup>4</sup> Sénéchal, *Compt. rend.*, 1913, 156, 552; 1914, 159, 243; Weinland and Krebs, *Zeitsch. anorg. Chem.*, 1906, 49, 157; Colson, *Compt. rend.*, 1906, 142, 402. The hydrate obtained as above described was formerly considered to contain  $18\text{H}_2\text{O}$ .

<sup>5</sup> Colson, *Compt. rend.*, 1905, 141, 1024.

<sup>6</sup> Wyruboff, *Bull. Soc. chim.*, 1902, [3], 27, 666.

<sup>7</sup> Colson, *Compt. rend.*, 1907, 144, 206.

<sup>8</sup> van Cleeff, *J. prakt. Chem.*, 1881, [2], 23, 58, 70; Étard, *Compt. rend.*, 1875, 80, 1306; 1877, 84, 1090.

<sup>9</sup> Colson, *Compt. rend.*, 1905, 140, 42, 372; 1907, 144, 637; 145, 250; Richards and Bonnet, *Zeitsch. physikal. Chem.*, 1904, 47, 29; Nicolardot, *Compt. rend.*, 1907, 145, 1338; Graham, *Amer. Chem. J.*, 1912, 48, 145; Colson, *Bull. Soc. chim.*, 1911, [4], 9, 862. Cf. Denham, *Zeitsch. anorg. Chem.*, 1908, 57, 361.

<sup>10</sup> Colson, *Bull. Soc. chim.*, 1907, [4], 1, 438.

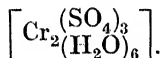
green chromium sulphates into three classes, which he denotes as trebly, doubly, and singly masked, according as three, two, or one acid radicles are unprecipitated by barium chloride solution in the cold. He suggests that the "masking" is due to the formation of such a

group as  $(\text{OH})\cdot\text{Cr}\cdot\text{HSO}_4$ . Moreover, the barium sulphate precipitated from a solution of the green, but not from one of the violet, salt adsorbs small quantities of a green, strongly basic chromium sulphate.

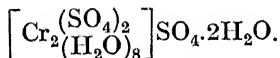
The green *hexahydrate*,  $\text{Cr}_2(\text{SO}_4)_3\cdot 6\text{H}_2\text{O}$ , or *Recoura's sulphate*,<sup>1</sup> is obtained by saturating a solution of chromic acid with sulphur dioxide at  $-4^\circ\text{C}$ . and immediately evaporating. The salt is soluble in water, yielding a green solution which gradually changes to violet.

When heated in dry air at  $80^\circ\text{C}$ . a less soluble *trihydrate*,  $\text{Cr}_2(\text{SO}_4)_3\cdot 3\text{H}_2\text{O}$ , results.

It is found<sup>2</sup> that attempts to precipitate the sulphate from Recoura's green sulphate are at first unsuccessful, but that after a time barium sulphate is deposited, the amount increasing at first rapidly, then gradually. The green solutions apparently tend towards a state of equilibrium which is a function of the temperature and concentration, and is the state towards which violet solutions of the same concentration gradually tend to pass. It is probable<sup>3</sup> that the composition of Recoura's green chromic sulphate may be expressed according to Werner's scheme by the formula



The green *decahydrate*,  $\text{Cr}_2(\text{SO}_4)_3\cdot 10\text{H}_2\text{O}$ , separates as an amorphous green hygroscopic mass when the green solution obtained by reducing chromic acid by sulphur dioxide at  $0^\circ\text{C}$ . is completely evaporated *in vacuo*. This compound differs from Recoura's sulphate in that the green colour of its solution is permanent, and one-third of its "sulphate" is precipitated by barium chloride. The constitution may probably be expressed thus:



The solution on boiling is hydrolysed in the same way as the violet solution, and the pentasulphate is formed. The freezing-point of the solution is unaltered by boiling, so that no change in the number of molecules present occurs.

Colson<sup>4</sup> considers that a cold solution of chromic sulphate is an equilibrium mixture of the violet sulphate with three green sulphates, to which he gave the formulæ  $\text{Cr}_2(\text{SO}_4)_3\cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}_2(\text{SO}_4)_2\cdot (\text{OH})\cdot (\text{HSO}_4)$ , and  $\text{Cr}_2(\text{SO}_4)(\text{OH})_2(\text{HSO}_4)_2$ . As to the green sulphate obtained by heating the solid violet salt, it has been stated<sup>5</sup> that it may exist in solution at the same temperature in two distinct molecular aggregations,  $[\text{Cr}_2(\text{SO}_4)_3]_2$  and  $\text{Cr}_2(\text{SO}_4)_3$ .

<sup>1</sup> Recoura, *Compt. rend.*, 1891, 112, 1439; 113, 857; *Ann. Chim. Phys.*, 1895, [7], 4, 494.

<sup>2</sup> Kling, Florentin, and Huchet, *Compt. rend.*, 1914, 159, 60.

<sup>3</sup> Colson, *Bull. Soc. chim.*, 1907, [4], 1, 438; Sénéchal, *Compt. rend.*, 1914, 159, 243.

<sup>4</sup> Colson, *Compt. rend.*, 1907, 144, 79.

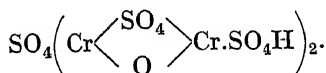
<sup>5</sup> Colson, *ibid.*, 1907, 144, 325. See also *Ann. Chim. Phys.*, 1907, [8], 12, 433.



By allowing a 0.5 N solution of chromium sulphate to stand until the state of equilibrium is attained, then evaporating *in vacuo* to the point of saturation, and adding excess of alcohol, Recoura<sup>1</sup> obtained a lilac-grey precipitate, which, after washing with ether, was found to contain  $18\text{H}_2\text{O}$ . On addition of barium chloride to its solution the whole of the sulphate ion was precipitated. After exposure to air for one day, however, it was found to have lost  $2\text{H}_2\text{O}$ , and the addition of barium chloride to its solution produced no precipitate. After remaining in a desiccator for some time, the compound contained only  $12\text{H}_2\text{O}$ . The constitution of these products has not been determined.

In fresh solutions of the green sulphate, the latter has the power of masking the sulphate ion in other metallic sulphates to the extent of several hundred molecules for each molecule of the green salt present, the actual amount depending on the age of the green solution, its concentration and degree of acidity.<sup>2</sup>

A *dihydroxypenta-sulphate*,  $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ , separates as an amorphous substance<sup>3</sup> when the green solution, obtained by shaking chromium hydroxide with a limited quantity of cold dilute sulphuric acid, is evaporated *in vacuo*. Only three of the five  $\text{SO}_4$  groups present are immediately precipitated by barium chloride, but the resistance to precipitation diminishes with rise in temperature or increase of concentration. The following constitution is suggested by Colson :



A number of *basic chromium sulphates* have been described<sup>4</sup>—(a)  $3\text{Cr}_2\text{O}_3\cdot 2\text{SO}_3\cdot 14\text{H}_2\text{O}$ ; (b)  $\text{Cr}_2\text{O}_3\cdot \text{SO}_3\cdot 6\text{H}_2\text{O}$ ; (c)  $2\text{Cr}_2\text{O}_3\cdot 3\text{SO}_3\cdot x\text{H}_2\text{O}$ ; (d)  $5\text{Cr}_2\text{O}_3\cdot 8\text{SO}_3\cdot x\text{H}_2\text{O}$ ; (e)  $\text{Cr}_2\text{O}_3\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$ ; (f)  $5\text{Cr}_2\text{O}_3\cdot 12\text{SO}_3\cdot x\text{H}_2\text{O}$ ; (g)  $7\text{Cr}_2\text{O}_3\cdot 5\text{SO}_3\cdot 25\text{H}_2\text{O}$ —as well as the acid sulphates,<sup>5</sup>  $2\text{Cr}_2(\text{SO}_4)_3\cdot \text{H}_2\text{SO}_4$  and  $2\text{Cr}_2(\text{SO}_4)_3\cdot 7\text{H}_2\text{SO}_4$ .

**Chromisulphuric Acids,**<sup>6</sup>  $\text{H}_2(\text{Cr}_24\text{SO}_4)$ ,  $\text{H}_4(\text{Cr}_25\text{SO}_4)$ , and  $\text{H}_6(\text{Cr}_26\text{SO}_4)$ , are obtained by drying at  $110^\circ$  to  $120^\circ$  C. the green residual mass after heating on the water-bath 1 molecule of chromic sulphate with 1, 2, or 3 molecules of sulphuric acid. The acids, which yield metallic salts, are stable amorphous powders when dry; in solution they gradually undergo dissociation. The suggestion has been made<sup>7</sup> that they may be regarded as negative colloids.

A number of double sulphates of trivalent chromium with other metals are known.

**Lithium Chromic Sulphate**,  $3\text{Li}_2\text{SO}_4\cdot \text{Cr}_2(\text{SO}_4)_3$ , forms<sup>8</sup> greyish-green, slightly soluble needles.

<sup>1</sup> Recoura, *Compt. rend.*, 1919, 169, 1163.

<sup>2</sup> Recoura, *ibid.*, 1922, 174, 1460.

<sup>3</sup> Colson, *ibid.*, 1905, 141, 119.

<sup>4</sup> (a) Schrötter, *Pogg. Annalen*, 1841, 53, 516; Schiff, *Annalen*, 1862, 124, 167; (b) Schiff, *loc. cit.*; (c) Bunsen, *Pogg. Annalen*, 1875, 155, 230; (d) Siewert, *Annalen*, 1863, 126, 97; (e) Schrötter, *loc. cit.*; Schiff, *loc. cit.*; Siewert, *loc. cit.*; (f) Siewert, *loc. cit.*; (g) Williamson, *J. Physical Chem.*, 1923, 27, 384.

<sup>5</sup> (a) Traube, *Annalen*, 1848, 66, 87; Siewert, *ibid.*, 1863, 126, 102; Kopp, *Compt. rend.*, 1844, 18, 1156; Schumann, *Annalen*, 1877, 187, 305; (b) Cross and Higgin, *Trans. Chem. Soc.*, 1882, 41, 113.

<sup>6</sup> Recoura, *Compt. rend.*, 1892, 114, 477; *Ann. Chim. Phys.*, 1895, [7], 4, 494; Whitney, *Zeitsch. physikal. Chem.*, 1896, 20, 44; Poizat, *Bull. Soc. chim.*, 1923, [4], 33, 1606.

<sup>7</sup> Martiñez-Strong, *Compt. rend.*, 1910, 150, 1172; *Anal. Fis. Quim.*, 1910, 8, 199.

<sup>8</sup> Wernicke, *Pogg. Annalen*, 1876, 159, 576.

**Sodium Chromic Sulphates.**—(a)  $\text{Na}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  is obtained by reduction of a mixture of sodium dichromate and sulphuric acid with alcohol; (b)  $3\text{Na}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$  forms green needles.<sup>1</sup>

**Potassium Chromic Sulphates.**—Several have been described:<sup>2</sup>  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ ;  $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ ; and  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Cr}_2\text{O}_3 \cdot \text{K}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$ , together with the more important chrome alum.

**Potassium Chromium Alum, "Chrome Alum,"**  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , first isolated by Mussin-Puschin,<sup>3</sup> is obtained by the reduction of a mixture of potassium dichromate and sulphuric acid by sulphurous acid,<sup>4</sup> alcohol, oxalic acid, etc.<sup>5</sup>

The aqueous solution (blue, with a reddish tinge, but becoming green at 50° to 70° C.) deposits violet octahedra; of the several forms in which chrome alum crystallises, including the rhombic dodecahedron, cube, and trapezohedron, the octahedron is the most stable.<sup>6</sup> The crystals have a density of about 1.84,<sup>7</sup> a specific heat of 0.324,<sup>8</sup> and a coefficient of expansion of 0.0000246.<sup>9</sup> The transformation of the violet to the green variety takes place at 78° C.,<sup>10</sup> the substance melting at 89° C.<sup>11</sup> to a green mass. Other physical constants have been determined,<sup>12</sup> and the absorption spectra of its aqueous solution studied.<sup>13</sup>

At ordinary temperatures, over concentrated sulphuric acid, chrome alum loses  $12\text{H}_2\text{O}$ ; on heating to 300° to 350° C. it becomes anhydrous, but decomposes in the air.<sup>14</sup> If heated much above 350° C. the residue is then insoluble in water.<sup>15</sup>

Chromium alum is soluble in water, 100 c.c. of water at 25° C. dissolving<sup>16</sup> 24.39 grams of the hydrated salt. The violet solution, on heating at 50° to 70° C., becomes green, and is then crystallisable with difficulty.<sup>17</sup> The violet solution, even at ordinary temperatures, slowly

<sup>1</sup> Wernicke, *loc. cit.*; Étard, *Compt. rend.*, 1877, 84, 1089.

<sup>2</sup> Wernicke, *Pogg. Annalen*, 1876, 159, 575; Recoura, *Compt. rend.*, 1892, 114, 477; Traube, *Annalen*, 1848, 66, 93; Étard, *loc. cit.*; Mitscherlich, *J. prakt. Chem.*, 1861, 83, 477.

<sup>3</sup> Mussin-Puschin, *Orell's Annalen*, 1801, 2, 267.

<sup>4</sup> It has been observed by Bassett, *Trans. Chem. Soc.*, 1903, 83, 692, that the reduction of potassium dichromate, potassium chromate, or chromium trioxide by sulphur dioxide yields 94 to 95 per cent. sulphate and 5 to 6 per cent. dithionate independently of the temperature; also that freshly reduced solutions give no reaction either for chromium or for sulphate ions.

<sup>5</sup> Schrötter, *Pogg. Annalen*, 1841, 53, 326; Fischer, *Kastner's Archiv*, 1828, 14, 164; 1829, 16, 216; Traube, *Annalen*, 1848, 66, 169; Lielegg, *Dingl. poly. J.*, 1873, 207, 321.

<sup>6</sup> Grinakowsky, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 802. See also Stiasny, *Dingl. poly. J.*, 1871, 202, 191; Polis, *Ber.*, 1880, 13, 360; Rammelsberg, *Pogg. Annalen*, 1854, 91, 351; Schiff, *Annalen*, 1858, 107, 81.

<sup>7</sup> Schiff, *loc. cit.*, gives 1.845; Playfair and Joule, *J. Chem. Soc.*, 1849, 1, 138, give 1.856; Kopp, *Annalen Suppl.*, 1864, 3, 294, gives 1.848; Pettersson, *Ber.*, 1876, 9, 156; 1882, 15, 1739, gives 1.842 at 20.8° C.; Gladstone, *Phil. Mag.*, 1885, [5], 20, 162, gives 1.817; Spring, *Ber.*, 1882, 15, 1254, gives 1.8293 at 0° C.; Dewar, *Chem. News*, 1905, 91, 216, gives 1.8278 at 0° C. and 1.834 at -188° C.

<sup>8</sup> Kopp, *loc. cit.*

<sup>9</sup> Spring, *Ber.*, 1882, 15, 1254; 1884, 17, 408. Cf. Dewar, *loc. cit.*

<sup>10</sup> Grinakowsky, *loc. cit.*

<sup>11</sup> Tilden, *Trans. Chem. Soc.*, 1884, 45, 409.

<sup>12</sup> Gladstone, *loc. cit.*; Gore, *Pogg. Annalen*, II. Beibl., 1878, 2, 430, 617.

<sup>13</sup> Ferrero and Nozari, *Atti R. Accad. Sci. Torino*, 1904-1905, 40, 453.

<sup>14</sup> Müller-Erzbach, *Zeitsch. physikal. Chem.*, 1888, 2, 545; Lescœur and Mathurin, *Bull. Soc. chim.*, 1888, [2], 50, 35; van Cleeff, *J. prakt. Chem.*, 1881, [2], 23, 72.

<sup>15</sup> Löwel, *Ann. Chim. Phys.*, 1855, [3], 44, 320.

<sup>16</sup> Locke, *Amer. Chem. J.*, 1901, 26, 174.

<sup>17</sup> de Boisbaudran, *Bull. Soc. chim.*, 1869, 12, 33; Gernez, *Compt. rend.*, 1874, 79, 1332; Franz, *J. prakt. Chem.*, 1872, [2], 5, 274; Jacquelin, *Compt. rend.*, 1847, 24, 440.

changes to green, the change being attended by increase of volume<sup>1</sup> and *vice versa*, irrespectively of concentration. The change appears to be due to hydrolysis, and the resulting basic chromic salts polymerise when the solution is heated, and, more slowly, even on standing.<sup>2</sup> The addition of alkali carbonate causes liberation of carbon dioxide due to the sulphuric acid formed, and precipitation occurs owing to coagulation of colloidal chromic hydroxide or of the polymerised basic salts. The amount of carbonate necessary to produce a permanent precipitate varies considerably with the age of the chrome-alum solution and with its method of preparation.<sup>3</sup>

Crystalline *rubidium* chromium alum has been described.<sup>4</sup>

With ammonium sulphate, chromic sulphate forms the double salts,  $3(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$  and  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$ , besides the alum,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . The former are obtained<sup>5</sup> on fusing oxides or certain other compounds of chromium with ammonium sulphate. The compound  $3(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$  forms green needles slightly attacked by water; the salt,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$ , identical with anhydrous ammonium chrome alum, forms hexagonal crystals.

**Ammonium Chromium Alum**,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , crystallises from a suitable mixture of solutions of its component salts in efflorescent octahedra of density 1.73,<sup>6</sup> melting at 100° C. with loss of  $18\text{H}_2\text{O}$ .

Ammonium chromium alum is soluble in water to the extent, at 25° C., of 21.21 grams of the hydrated salt in 100 c.c. of water,<sup>7</sup> yielding a bluish-violet solution which becomes green at 70° to 80° C.<sup>8</sup> A study of the equilibria existing in such a solution makes it appear that the change from the violet to the green modification does not take place at all at 0° C., but that at 40° C. the solution contains about 40 per cent. of the green alum.<sup>9</sup>

**Hydroxylamine Chromium Alum**,  $(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , is stated<sup>10</sup> to exist.

**Hydrazine Chromium Alum**,  $(\text{N}_2\text{H}_4)_2\text{H}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , forms violet octahedral crystals, soluble in water.<sup>11</sup>

Compounds of the green chromium sulphate with chromic acid have been prepared,<sup>12</sup> viz.  $\text{H}_2[\text{CrO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3]$ ,  $\text{H}_4[(\text{CrO}_4)_2 \cdot \text{Cr}_2(\text{SO}_4)_3]$ , and  $\text{H}_6[(\text{CrO}_4)_3 \cdot \text{Cr}_2(\text{SO}_4)_3]$ .

**Sulphochromic Acid**,  $\text{Cr}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , and certain of its salts,

<sup>1</sup> Mohr, *Ber.*, 1871, 4, 318.

<sup>2</sup> Meunier, *J. Soc. Leather Trades Chem.*, 1921, 5, 103.

<sup>3</sup> Meunier and Caste, *Compt. rend.*, 1921, 172, 1488. For data of work on chrome-alum solutions see de Boisbaudran, *loc. cit.*; *Compt. rend.*, 1874, 79, 1491; van Cleeff, *loc. cit.*; Krüger, *Pogg. Annalen*, 1844, 61, 218; Siewert, *Annalen*, 1863, 126, 98; Löwel, *J. Pharm.*, 1845, [3], 7, 321; Tishborne, *Bull. Soc. chim.*, 1872, [2], 17, 25; Recoura, *ibid.*, 1891, [3], 7, 909. See also von Hauer, *Wied. Annalen*, 1894, 53, 2, 221; Klocke, *Zeitsch. Kryst. Min.*, 1877, 2, 126; Spring, *Ber.*, 1882, 15, 1254; Schumann, *Annalen*, 1877, 187, 307; Jean, *Compt. rend.*, 1869, 68, 198; Lumière and Seyewitz, *Bull. Soc. chim.*, 1902, [3], 27, 1073.

<sup>4</sup> Pettersson, *Acta Soc. Sci. Upsala*, 1876, [3], 9; *Ber.*, 1876, 9, 1559.

<sup>5</sup> Klobb, *Bull. Soc. chim.*, 1892, [3], 9, 663.

<sup>6</sup> Schrötter, *Pogg. Annalen*, 1841, 53, 526, gives 1.736 at 21° C.; Pettersson gives 1.728 at 20° C.; Gladstone, *Phil. Mag.*, 1885, [5], 20, 162, gives 1.719.

<sup>7</sup> Locke, *Amer. Chem. J.*, 1901, 26, 174.

<sup>8</sup> Schrötter, *Pogg. Annalen*, 1841, 53, 526; Koppel, *Ber.*, 1906, 39, 3738.

<sup>9</sup> Koppel, *loc. cit.*

<sup>10</sup> Meyeringh, *Ber.*, 1877, 10, 1946.

<sup>11</sup> Sommer, *Zeitsch. anorg. Chem.*, 1916, 94, 70.

<sup>12</sup> Recoura, *loc. cit.*

**Chromic Selenide,  $\text{Cr}_2\text{Se}_3$ .**—This compound is produced as a maroon-coloured amorphous powder by heating the sesquioxide in selenium vapour and hydrogen or nitrogen; <sup>1</sup> by the action of hydrogen selenide upon chromic chloride, it is obtained in the crystalline condition. The double selenide of potassium and chromium,  $\text{K}_2\text{Cr}_2\text{Se}_4$ , is prepared as dark green hexagonal crystals, which are readily soluble in nitric acid but insoluble in hydrochloric acid, by heating to redness a mixture of potassium cyanide, selenium, and chromic oxide.<sup>2</sup>

**Chromic Selenite,  $\text{Cr}_2\text{O}_3 \cdot 3\text{SeO}_2$ ,** is precipitated as a pale green substance, insoluble in water, when potassium selenite is added to a boiling solution of chromic chloride. If the latter contain excess of hydrochloric acid, the sparingly soluble diselenite,  $\text{Cr}_2\text{O}_3 \cdot 6\text{SeO}_2$ , is also formed.<sup>3</sup>

**Chromic Selenate** itself has not been isolated, but double salts (which are alums) of the type  $\text{Cr}_2(\text{SeO}_4)_3 \cdot \text{R}_2\text{SeO}_4 \cdot 24\text{H}_2\text{O}$  are known,<sup>4</sup> as well as those of the type  $\text{Cr}_2(\text{SeO}_4)_3 \cdot \text{R}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ .

The existence of both **chromic tellurite** and **chromic tellurate** finds mention, but the study of these compounds is most superficial.

**Chromotellurates,  $2\text{R}'_2\text{O} \cdot 4\text{CrO}_3 \cdot \text{TeO}_3$ ,** of sodium, potassium, and ammonium, have been prepared <sup>6</sup> by spontaneous evaporation of an aqueous solution containing the corresponding dichromate (1 molecule), chromium trioxide (2 molecules), and telluric acid (1 molecule).

**Chromic Chromate**, or chromium dioxide,  $\text{CrO}_2$ , has already been dealt with (p. 39).

**Ammonium and potassium chromimolybdates**, salts of chromimolybdic acid,  $\text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 28\text{H}_2\text{O}$ , have been prepared <sup>7</sup> (see also p. 142).

**Chromic Tungstates**, see p. 217.

**Chromic Borotungstate,** <sup>8</sup>  $2\text{Cr}_2\text{O}_3 \cdot 3(\text{WO}_3 \cdot \text{B}_2\text{O}_3) \cdot 6\text{H}_2\text{O} + 68\text{aq}$ , and tungsten chromite,  $\text{Cr}_2\text{O}_3 \cdot 5\text{WO}_3$ ,<sup>9</sup> have been described.

## CHROMIUM AND NITROGEN.

**Chromium Nitrides.**—The absorption of nitrogen by finely divided chromium begins at  $800^\circ$  to  $820^\circ$  C.; the metal does not melt; the product, which is distinctly magnetic, contains 8 per cent. of nitrogen.<sup>10</sup> On heating to  $850^\circ$  C. in ammonia, chromium yields a dull black *nitride*,  $\text{Cr}_3\text{N}_2$ , containing small quantities of unchanged chromium.<sup>11</sup>

A nitride of chromium,  $\text{CrN}$ , is formed when the violet sesquioxide is heated in a current of dry ammonia,<sup>12</sup> when chromic and ammonium

<sup>1</sup> Moissan, *Compt. rend.*, 1880, 90, 817.

<sup>2</sup> Milbauer, *Zeitsch. anorg. Chem.*, 1904, 42, 450.

<sup>3</sup> Taquet, *Compt. rend.*, 1883, 97, 1435.

<sup>4</sup> Wohlwill, *Annalen*, 1860, 114, 162; Fabre, *Compt. rend.*, 1887, 105, 114; Pettersson, *Ber.*, 1873, 6, 1466.

<sup>5</sup> von Gerichten, *Annalen*, 1873, 168, 214.

<sup>6</sup> Berg, *Compt. rend.*, 1911, 152, 1587; *Bull. Soc. chim.*, 1911, [4], 9, 583.

<sup>7</sup> Hall, *J. Amer. Chem. Soc.*, 1907, 29, 692; Struve, *J. prakt. Chem.*, 1854, 61, 449.

<sup>8</sup> Klein, *Compt. rend.*, 1880, 91, 415; *Ann. Chim. Phys.*, 1883, [5], 28, 350, 432.

<sup>9</sup> Smith, *J. Amer. Chem. Soc.*, 1893, 15, 151.

<sup>10</sup> Shukoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 457. See du Jassonnoix, *Compt. rend.*, 1907, 144, 915; Briegleb and Geuther, *Annalen*, 1862, 123, 239.

<sup>11</sup> Henderson and Galletly, *J. Soc. Chem. Ind.*, 1908, 27, 387; Baur and Voerman, *Zeitsch. physikal. Chem.*, 1905, 52, 467.

<sup>12</sup> Schrötter, *Annalen*, 1841, 37, 148; Ufer, *ibid.*, 1859, 112, 281.

chlorides are heated together in hydrogen,<sup>1</sup> or when chromium amalgam is distilled in nitrogen.<sup>2</sup> On heating the nitride in hydrogen no reduction is observed;<sup>3</sup> the brown insoluble powder, on heating in air, burns to nitrogen and chromic oxide, and on heating in ammonia is said<sup>4</sup> to yield the nitride  $\text{Cr}_3\text{N}$ .

**Chromium Azide,  $\text{Cr}(\text{N}_3)_3$ ,** is obtained as a dark green amorphous mass by prolonged treatment of a solution of crystallised chromium nitrate in absolute alcohol with anhydrous sodium sulphate, and evaporation of the filtered liquid with the requisite quantity of sodium azide in a vacuum.<sup>5</sup> The azide is very hygroscopic, and if its alcoholic solution is not thoroughly dry, partial hydrolysis occurs, basic azides of composition  $\text{Cr}(\text{OH})(\text{N}_3)_2$  and  $\text{Cr}(\text{OH})_2\text{N}_3$  being formed. A double compound with sodium,  $\text{Cr}(\text{N}_3)_3 \cdot 3\text{NaN}_3$ , has been obtained in the form of green crystals.

**Chromic Nitrate,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,** obtained by warming nitric acid with excess of chromic hydroxide (this giving a basic salt) and crystallising after the addition of a sufficient excess of nitric acid, forms purple rhombic prisms, melting at  $36.5^\circ \text{C}$ . and soluble in alcohol. The salt decomposes at  $100^\circ \text{C}$ .<sup>6</sup>

More recent investigations<sup>7</sup> have shown that when strongly heated chromic oxide (which, contrary to common statements, is not entirely insoluble in acids) is dissolved in hot concentrated nitric acid of density 1.4, the hydrate  $\text{Cr}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$  crystallises on cooling. The dark brown crystals are prismatic:

$$a : b : c = 1.4250 : 1 : 1.1158 ; \beta = 93^\circ 10'.$$

In contact with dry air water is lost, the residue having the composition  $\text{Cr}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$ .<sup>8</sup> Violet crystals of the hydrate with  $15\text{H}_2\text{O}$ , melting at  $100^\circ \text{C}$ ., have been prepared.<sup>9</sup>

Two *basic nitrates*,  $\text{Cr}(\text{NO}_3)_2\text{OH}$  and  $\text{Cr}(\text{NO}_3)(\text{OH})_2$ , are known<sup>10</sup> as green amorphous substances.

The **chloronitrates**,  $\text{Cr}(\text{NO}_3)_2\text{Cl}$  and  $\text{Cr}(\text{NO}_3)\text{Cl}_2$ , have been prepared, together with the **sulphatonitrate**,  $\text{Cr}(\text{NO}_3)\text{SO}_4$ .<sup>11</sup>

## CHROMIUM AND PHOSPHORUS.

**Chromous Phosphide or Chromium Monophosphide,  $\text{CrP}$ ,** can be obtained by heating chromic chloride either with phosphorus in presence of hydrogen<sup>12</sup> or in gaseous hydrogen phosphide;<sup>13</sup> by heating a mixture of finely divided chromium and copper phosphide in the electric furnace, the copper being removed from the product by treat-

<sup>1</sup> Uhrlaub, *Verbindungen einiger Metalle mit Stickstoff*, Göttingen, 1859.

<sup>2</sup> Férée, *Bull. Soc. chim.*, 1902, [3], 25, 618; Guntz, *ibid.*, 1902, [3], 27, 1190; *Compt. rend.*, 1902, 135, 738.

<sup>3</sup> Baur and Voerman, *loc. cit.*

<sup>4</sup> Uhrlaub, *loc. cit.*; Baur, *Ber.*, 1901, 34, 2385.

<sup>5</sup> Oliveri-Mandala and Comella, *Gazzetta*, 1922, 52, I, 112.

<sup>6</sup> Ordway, *Amer. J. Sci.*, 1850, [2], 9, 30.

<sup>7</sup> Jovitschitsch, *Monatsh.*, 1909, 30, 47; 1912, 33, 9; Halse, *Chem. Zeit.*, 1912, 36, 962.

<sup>8</sup> Jovitschitsch, *loc. cit.*

<sup>9</sup> Halse, *loc. cit.*

<sup>10</sup> Ordway, *loc. cit.*; Schiff, *Annalen*, 1862, 124, 170; Siewert, *ibid.*, 1863, 126, 99.

<sup>11</sup> Schiff, *loc. cit.*

<sup>12</sup> Granger, *Compt. rend.*, 1897, 124, 190; *Ann. Chim. Phys.*, 1898, [7], 14, 38.

<sup>13</sup> Rose, *Pogg. Annalen*, 1832, 24, 333.

ment with nitric acid;<sup>1</sup> or by the reduction of chromic phosphate by strongly heating with charcoal. It is a grey crystalline solid, having the appearance of graphite; density 5.71.<sup>1</sup> It is unaffected by ordinary acids, but will dissolve in a mixture of nitric and hydrofluoric acids. When heated in air it oxidises slowly. Chlorine attacks it with incandescence. It is decomposed by fused caustic potash, hydrogen being evolved and potassium chromate formed.

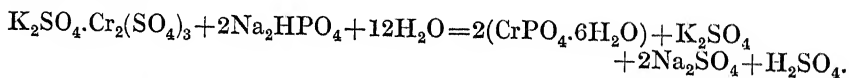
**Chromium Sesquiphosphide**,  $\text{Cr}_2\text{P}_3$ , has been prepared<sup>2</sup> by heating finely divided chromium with an excess of red phosphorus at  $700^\circ \text{C}$ . in a sealed exhausted tube. It is a grey powder, insoluble in acids. On heating at  $440^\circ \text{C}$ . in a current of hydrogen, the monophosphide is formed.

**Chromic Hypophosphite**,  $\text{Cr}(\text{H}_2\text{PO}_2)_3 \cdot 2\text{H}_2\text{O}$ , is obtained<sup>3</sup> by evaporating down on a water-bath a solution of freshly precipitated chromic hydroxide in hypophosphorous acid, washing the green mass obtained with water and drying over sulphuric acid. A *basic hypophosphite*,  $2\text{Cr}(\text{OH})(\text{H}_2\text{PO}_2)_2 \cdot 3\text{H}_2\text{O}$ , is obtained as a dark green amorphous fissured mass by the reaction of barium hypophosphite with chromic sulphate and evaporation of the filtrate.<sup>4</sup> When heated to  $200^\circ \text{C}$ . it gives off water, and is then insoluble in water and in dilute acids.

**Chromium Phosphite**<sup>5</sup> is precipitated from aqueous chromic chloride by the addition of an alkali phosphite, heat being necessary for complete precipitation; it is partly separated when phosphorus trichloride, dissolved in water and neutralised with ammonia, is added to chromic chloride, the phosphite remaining in solution giving a green colour to the liquid. When dry, it is a loose grey powder, decomposed by heat with liberation of pure hydrogen.

**Chromous Orthophosphate**,  $\text{Cr}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , is the abundant blue gelatinous precipitate obtained when ordinary sodium phosphate is added to chromous chloride solution. It is readily soluble in acids, and on exposure to air rapidly changes to the green chromic salt.<sup>6</sup> It does not form double salts with ammonium phosphate.<sup>7</sup>

**Chromic Orthophosphates**.—*Violet chromic phosphate*,  $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$ , is produced as a lavender amorphous precipitate when cold solutions of equal weights of chrome alum and ordinary sodium phosphate are mixed:<sup>8</sup>



If the precipitate is allowed to remain for a day or two in contact with the solution, it becomes dark violet and crystalline; it may then be washed by decantation and dried in the air. The product is slightly soluble in water; readily soluble in sulphuric and hydrochloric acids;

<sup>1</sup> Maronneau, *Compt. rend.*, 1900, 130, 656.

<sup>2</sup> Dieckmann and Hanf, *Zeitsch. anorg. Chem.*, 1914, 86, 291.

<sup>3</sup> Mawrow and Zonew, *ibid.*, 1915, 93, 311.

<sup>4</sup> Wurtz, *Ann. Chim. Phys.*, 1846, [3], 16, 196.

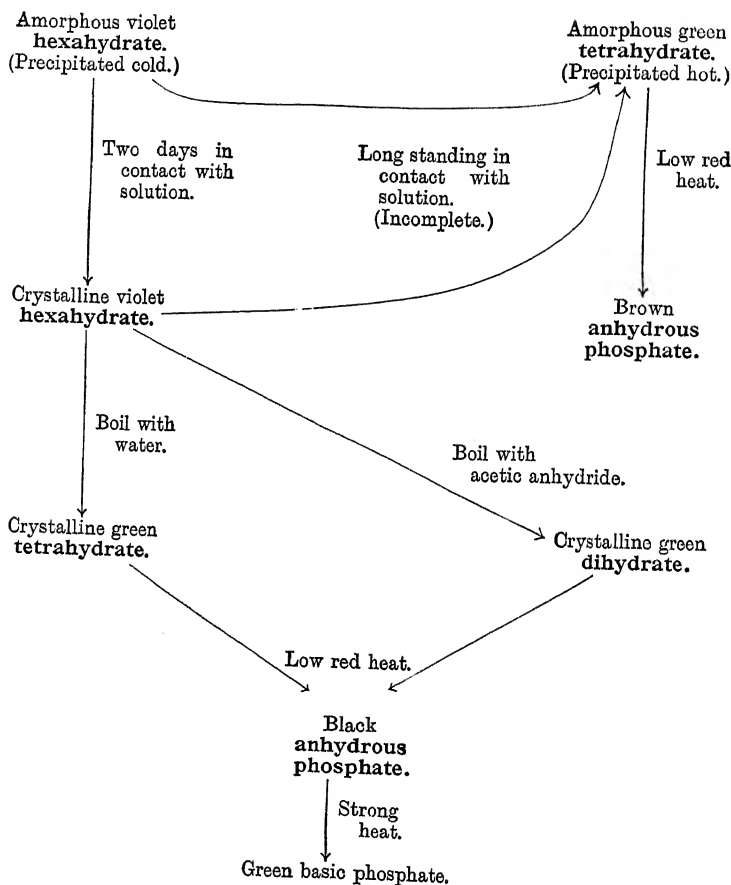
<sup>5</sup> Rose, *Pogg. Annalen*, 1827, 9, 40.

<sup>6</sup> Moberg, *J. prakt. Chem.*, 1848, 44, 322.

<sup>7</sup> Moissan, *Ann. Chim. Phys.*, 1882, [5], 25, 415.

<sup>8</sup> Joseph and Rae, *Trans. Chem. Soc.*, 1917, 111, 196. See also Schiff, *Zeitsch. anorg. Chem.*, 1905, 43, 304; Dowling and Plunkett, *Chem. Gazette*, 1858, p. 220; Rammelsberg, *Pogg. Annalen*, 1846, 68, 383; Vauquelin, *Ann. Chim.*, 1809, [1], 70, 70.

The relations between the various chromic orthophosphates may be indicated diagrammatically as follows :<sup>1</sup>



*Acid Chromic Orthophosphate*,  $\text{CrH}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , has been described.<sup>2</sup> It forms asymmetric crystals of the colour of the chrome alums; stable in air. Vauquelin<sup>3</sup> obtained an emerald green uncrystallisable solution by acting upon the hydrated sesquioxide of chromium with aqueous phosphoric acid.

Several *double phosphates* have been described. Ammonium chromic phosphate,  $(\text{NH}_4)_2\text{HPO}_4 \cdot 2\text{CrPO}_4 \cdot 3\text{H}_2\text{O}$ , is obtained as a green precipitate<sup>4</sup> when diammonium hydrogen phosphate is added in large excess to a solution of chromic chloride containing hydrochloric acid, but not too strongly acid. If the acidity is reduced until there is very little or no hydrochloric acid present, the basic compound,  $5(\text{NH}_4)\text{H}_2\text{PO}_4 \cdot 2\text{CrPO}_4 \cdot 4\text{Cr}(\text{OH})_3$ , is formed. Sodium chromic phos-

<sup>1</sup> See Joseph and Rae, *Trans. Chem. Soc.*, 1917, III, 196.

<sup>2</sup> Haushofer, *Zeitsch. Kryst. Min.*, 1882, 7, 263.

<sup>3</sup> Vauquelin, *Ann. Chim.*, 1809, [1], 70, 70.

<sup>4</sup> Cohen, *J. Amer. Chem. Soc.*, 1907, 29, 1194.

phate,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{CrPO}_4 \cdot 5\text{H}_2\text{O}$ , is precipitated under certain conditions<sup>1</sup> when solutions of chromium salts are boiled with sodium phosphate and acetic acid (*cf.* p. 87), but on repeatedly washing the precipitate with water a basic salt is formed.

**Chromous Metaphosphate,  $\text{Cr}(\text{PO}_3)_2$ .**—Attempts to produce this compound by the action of fused metaphosphoric acid on chromium or on chromous salts have not been successful,<sup>2</sup> although the method succeeds for the ferrous analogue.<sup>3</sup>

**Chromic Metaphosphate,  $\text{Cr}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$  or  $\text{Cr}(\text{PO}_3)_3$ ,** is prepared by evaporating a solution of chromium hydroxide in excess of aqueous orthophosphoric acid, and heating the residue for some hours at about  $300^\circ \text{C}$ .; <sup>4</sup> or by fusion of chromium sesquioxide with metaphosphoric acid; <sup>5</sup> or by heating the sulphate with metaphosphoric acid.<sup>6</sup> When prepared by the first method it is freed from phosphoric acid by boiling with water, and then dried. It is a fine green powder, yielding orthorhombic crystals isomorphous with the metaphosphates of iron, aluminium, and uranium.<sup>5</sup> It is insoluble in water and acids. On heating it turns brown, but regains its green colour on cooling. The dry metaphosphate has a density of 2.9; <sup>7</sup> its molecular volume is 195.

**Chromic Pyrophosphate,  $2\text{Cr}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$  or  $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ ,** is obtained when sodium pyrophosphate is added to a boiling solution of chrome alum,<sup>8</sup> or when fused sodium metaphosphate is saturated with chromium sesquioxide at a high temperature.<sup>9</sup> It yields small, pale green, transparent, rhomboclinic prisms, of density 3.2 at  $20^\circ \text{C}$ . It is insoluble in ordinary acids, but will dissolve in water acidified with sulphuric acid, from which solution it is deposited in an amorphous form on boiling; it is soluble in solutions of sodium pyrophosphate in strong mineral acids, and in a solution of caustic potash. It is not altered by ammonium sulphide.<sup>10</sup> On heating to  $100^\circ \text{C}$ . its colour deepens, but on ignition it turns a paler green.<sup>8</sup> *Double salts* with potassium and sodium have been obtained.<sup>11</sup>

**Complex Pyrophosphates,** containing chromium in the negative radicle, have been prepared.<sup>12</sup> They may be considered as salts of chromi-pyrophosphoric acid,  $\text{H}(\text{CrP}_2\text{O}_7)$ , and are obtained by dropping a solution of chromium sesquioxide in cold concentrated hydrochloric acid into saturated solutions of alkali pyrophosphates.

**Ammonium Chromi-pyrophosphate,  $\text{NH}_4(\text{CrP}_2\text{O}_7) \cdot 6\text{H}_2\text{O}$ ,** yields grey microscopic columns.

**Potassium Chromi-pyrophosphate,  $\text{K}(\text{CrP}_2\text{O}_7) \cdot 5\text{H}_2\text{O}$ ,** is pale green.

<sup>1</sup> Cohen, *loc. cit.*

<sup>2</sup> Colani, *Compt. rend.*, 1914, 158, 794.

<sup>3</sup> Ludert, *Zeitsch. anorg. Chem.*, 1894, 5, 37. See this series, Vol. IX., Part II., p. 187.

<sup>4</sup> Maddrell, *Mem. Chem. Soc.*, 1845–1847, 3, 273.

<sup>5</sup> Hautefeuille and Margottet, *Compt. rend.*, 1883, 96, 849.

<sup>6</sup> Johnson, *Ber.*, 1889, 22, 978.

<sup>7</sup> Joseph and Rae, *Trans. Chem. Soc.*, 1917, III, 196, give 2.93; Johnson, *loc. cit.* gives 2.974.

<sup>8</sup> Schwarzenberg, *Annalen*, 1848, 65, 2, 149.

<sup>9</sup> Ouvrard, *Ann. Chim. Phys.*, 1889, [6], 16, 289.

<sup>10</sup> Persoz, *Annalen*, 1848, 65, 170.

<sup>11</sup> Walroth, *Ber.*, 1883, 16, 3059; Ouvrard, *loc. cit.*; Persoz, *loc. cit.*

<sup>12</sup> Rosenheim and Triantaphyllides, *Ber.*, 1915, 48, 582.



**Sodium Chromi-pyrophosphate**,  $\text{Na}(\text{CrP}_2\text{O}_7) \cdot 8\text{H}_2\text{O}$ , is grey, but on standing a few days changes to the pale green pentahydrate.

Other complex phosphates have been described.<sup>1</sup> Plessy's *Chrome Green* is a green pigment prepared by adding calcium phosphate to potassium dichromate and treating the mixture with sugar. It is probably not a definite compound, but a mixture of the phosphates of chromium, calcium, and potassium with chromium oxide and water.<sup>2</sup> Complex salts have been prepared<sup>3</sup> by the condensation of alkali phosphates with chromates and dichromates. For example, the *ammonium* compound,  $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 8\text{CrO}_3 \cdot \text{H}_2\text{O}$ , has been prepared by crystallisation from a solution containing molecular proportions of ammonium dichromate and phosphorus pentoxide, or of ammonium dihydrogen phosphate and chromium trioxide. A good yield of deep red crystals was obtained. The *potassium* compound,  $2\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 4\text{CrO}_3 \cdot \text{H}_2\text{O}$ , was obtained by the evaporation of a solution containing molecular proportions of potassium dichromate and phosphorus pentoxide, but in this case some crystals of potassium dichromate were first formed.

**Chromous Thiophosphite**,  $\text{Cr}_3(\text{PS}_3)_2$ , is prepared<sup>4</sup> by heating metallic chromium with a mixture of sulphur and red phosphorus to a cherry-red heat in a closed vessel for twenty hours. It yields black, hexagonal, microscopic crystals, possessing metallic lustre.

**Chromous Thiopyrophosphite**,  $\text{Cr}_2\text{P}_2\text{S}_6$ , called by Ferrand a *thiohypophosphate*, has been obtained by heating the metal with sulphur and red phosphorus as in the preparation of the preceding salt, the proportions of the elements being varied, and the heating continued for twenty-four hours. It crystallises in lustrous, black, hexagonal lamellæ, which are insoluble in nitric acid and only slightly soluble in aqua regia.

**Chromous Thiopyrophosphate**,  $\text{Cr}_2\text{P}_2\text{S}_7$ , is obtained<sup>5</sup> as minute, black, hexagonal lamellæ by the same method as the two preceding salts. It is very resistant to the action of nitric acid or aqua regia, but is decomposed by water or moist air.

Suitable mixtures for the above preparations are as follows :

	Cr.	S.	P.
$\text{Cr}_3(\text{PS}_3)_2$ . . .	1.56	1.92	0.62
$\text{Cr}_2\text{P}_2\text{S}_6$ . . .	2.08	3.84	1.24
$\text{Cr}_2\text{P}_2\text{S}_7$ . . .	1.04	2.24	0.62

**Double Compounds with the Halides of Phosphorus.**—When chromic chloride or chromyl chloride is heated with excess of phosphorus pentachloride in a sealed tube, a violet crystalline compound, having the composition  $\text{PCl}_5 \cdot \text{CrCl}_3$ , results.<sup>6</sup>

<sup>1</sup> Arnaudon, *Rép. Chim. appl.*, i, 201; Plessy, *Dingl. poly. J.*, 1863, 167, 397.

<sup>2</sup> Köthe, *Dingl. poly. J.*, 1874, 214, 59.

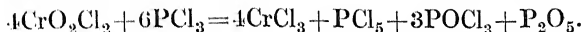
<sup>3</sup> Friedheim, *Zeitsch. anorg. Chem.*, 1894, 6, 273.

<sup>4</sup> Ferrand, *Compt. rend.*, 1896, 122, 621; *Ann. Chim. Phys.*, 1899, [7], 17, 419.

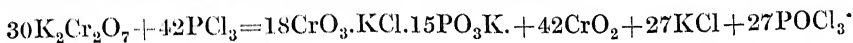
<sup>5</sup> Ferrand, *Compt. rend.*, 1896, 122, 886.

<sup>6</sup> Cronander, *Upsala Univers. Arsskr.*, 1873; *Ber.*, 1873, 6, 1466; Weber, *Pogg. Annalen*, 1859, 107, 386.

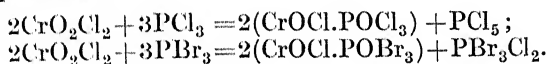
Michaelis<sup>1</sup> noticed that when small quantities of chromyl chloride and phosphorus trichloride were brought together, a vigorous reaction occurred accompanied by a hissing noise and evolution of light (see p. 24). He represented the change by the following equation :



On heating potassium dichromate with phosphorus trichloride in a sealed tube at 166° C. the following reaction occurred :



The action of the phosphorus halides on chromyl chloride has been studied more recently by Fry and Donnelly,<sup>2</sup> who worked with non-aqueous solvents. The explosive nature of the reactions was moderated by bringing the substances together in solutions of 0.2 molecular concentration in anhydrous carbon tetrachloride. With phosphorus trichloride and tribromide, solid double compounds were produced according to the equations :



The double compounds are extremely deliquescent, and react with water, with development of heat, according to the equation :



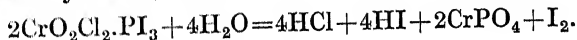
On ignition, the compounds  $\text{CrOCl}$  (or  $\text{Cr}_2\text{O}_3 \cdot \text{CrCl}_3$ ) and  $\text{CrOBr}$  (or  $\text{Cr}_2\text{O}_3 \cdot \text{CrBr}_3$ ) are produced.

Chromyl chloride and phosphorus pentachloride, under the same conditions, yield an additive compound,  $\text{CrO}_2\text{Cl}_2 \cdot \text{P}_2\text{O}_5$ , as a yellowish-red powder, which is easily decomposed by water.

With phosphorus pentabromide a substance is obtained which appears to be a mixture of the compounds  $\text{CrOCl} \cdot \text{POBr}_3$  and  $\text{CrO}_2\text{Cl}_2 \cdot \text{PBr}_5$ . This is probably due to the fact that phosphorus pentabromide is partly dissociated to tribromide in carbon tetrachloride solution.

With phosphorus di-iodide a brown additive compound,  $\text{CrO}_2\text{Cl}_2 \cdot \text{PI}_2$ , is obtained. It is readily decomposed by water, giving free iodine and a solution containing chromic, phosphate, chloride, and iodide ions.

Phosphorus tri-iodide under similar conditions gives the additive compound  $\text{CrO}_2\text{Cl}_2 \cdot \text{PI}_3$ , which is a purplish-red powder when dry. It is decomposed by water, thus :



#### CHROMIUM AND ARSENIC.

**Chromous Arsenide,  $\text{CrAs}$ ,** has been obtained<sup>3</sup> by heating the sesqui-arsenide in hydrogen at 480° to 500° C. Its density at 16° C. is 6.35. It is insoluble in acids.

**Chromium Sesqui-arsenide,  $\text{Cr}_2\text{As}_3$ ,** is prepared<sup>3</sup> by heating finely divided chromium with excess of arsenic at 700° C. in a sealed exhausted tube, the product being powdered and again heated. The

<sup>1</sup> Michaelis, *Jenaische Zeitsch.*, 1871, 7, 110; *Jahresber.*, 1871, p. 248.

<sup>2</sup> Fry and Donnelly, *J. Amer. Chem. Soc.*, 1916, 38, 1923; 1918, 40, 478.

<sup>3</sup> Dieckmann and Hanf, *Zeitsch. anorg. Chem.*, 1914, 86, 291.

resulting compound is not changed in composition by prolonged heating in hydrogen at  $400^{\circ}\text{C.}$ , but above that temperature it loses arsenic and passes to the monoarsenide. Chromium sesqui-arsenide is a grey powder, of density 6.2 at  $22^{\circ}\text{C.}$ ; it is insoluble in acids.

**Chromic Arsenite**,  $\text{CrAsO}_3$ , separates as a dark green powder when a concentrated solution of pure chromic acid is boiled for some time with a saturated solution of arsenious acid.<sup>1</sup>

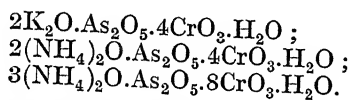
**Chromic Arsenate**,  $\text{CrAsO}_4$ , is formed as an apple-green precipitate when potassium arsenate is added to a solution of a chromic salt.

*Double arsenates* of chromium with the alkali metals have been described. When aqueous arsenious acid is added to a solution of potassium chromate, the liquid becomes green and soon coagulates to a tremulous jelly, which when dried at  $100^{\circ}\text{C.}$  yields a substance whose empirical formula is  $4\text{K}_2\text{O} \cdot 3\text{Cr}_2\text{O}_3 \cdot 3\text{As}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ .<sup>2</sup> The double arsenates,  $\text{K}_3\text{Cr}_2(\text{AsO}_4)_3$  and  $\text{Na}_3\text{Cr}_2(\text{AsO}_4)_3$ , have been prepared<sup>3</sup> by the addition of chromium sesquioxide to the fused alkali meta-arsenate. Crystallisation is accelerated by the addition of alkali chloride. Both compounds yield green transparent crystals. In the case of the potassium salt more than 7, and of the sodium salt more than 8, per cent. of the sesquioxide must be employed or a pyroarsenate is produced (see below).

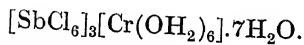
**Chromium Pyroarsenate**,  $\text{Cr}_4(\text{As}_2\text{O}_7)_3$ ,<sup>3</sup> is produced when a small quantity of chromium sesquioxide is fused at a low temperature with sodium or potassium meta-arsenate. It yields green transparent prisms, sometimes elongated, sometimes flattened, with oblique extinctions; insoluble in dilute acids.

**Chromic Thioarsenite**,  $2\text{Cr}_2\text{S}_3 \cdot 3\text{AsS}_3$ , and chromic thioarsenate have been described by Berzelius.<sup>4</sup>

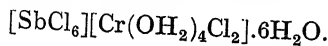
By allowing solutions containing molecular proportions of alkali arsenate and chromic oxide, or of arsenic pentoxide and alkali chromate or dichromate, to crystallise, the following *complex salts* have been obtained: <sup>5</sup>



**Chromium Chlorantimonate or Chromium Metantimonichloride**,  $\text{Cr}(\text{SbCl}_6)_3 \cdot 13\text{H}_2\text{O}$ , has been obtained<sup>6</sup> as grey-violet, flat, hygroscopic needles by the action of antimony pentachloride on chromic chloride. The salt may be formulated<sup>7</sup> according to Werner's scheme as follows:



**Chromium Orthoantimonichloride**,  $\text{CrSbCl}_6 \cdot 10\text{H}_2\text{O}$ , was obtained by Weinland and Feige in the form of grey hygroscopic plates, but Pfeiffer obtained it as dark green crystals, and showed that it was not a derivative of the ortho-acid, but should be formulated thus:



<sup>1</sup> Neville, *Chem. News*, 1876, 34, 220.

<sup>2</sup> Schweitzer, *J. prakt. Chem.*, 1846, 39, 267.

<sup>3</sup> Lefèvre, *Compt. rend.*, 1890, **III**, 36.

<sup>4</sup> Berzelius, *Traité de Chimie*, 1831, 4, 509.

<sup>5</sup> Friedheim, *Zeitsch. anorg. Chem.*, 1894, 6, 273.

<sup>6</sup> Weinland and Feige, *Ber.*, 1903, 36, 244.

<sup>7</sup> Pfeiffer, *Zeitsch. anorg. Chem.*, 1903, 36, 349.

## CHROMIUM AND CARBON.

**Carbides.**—That a carbide may be produced during the reduction of chromic oxide by carbon, especially if excess of the latter be used, was first suspected by Deville. In the reduction of an oxide of ruthenium containing oxide of chromium in a carbon crucible, beautiful glittering crystals were obtained.<sup>1</sup>

**Tetrachromium Carbide, Chromium Subcarbide,  $\text{Cr}_4\text{C}$ .**—In the preparation of chromium in the electric furnace, Moissan sometimes saw large metallic ingots covered with reddish-brown needles, often 1 to 2 cm. long, and of density 6.75. Similar glittering needles were also met with in the geodes which formed in the middle of the melt of chromium. Moissan attributed to them the formula  $\text{Cr}_4\text{C}$ , but this has not been confirmed.<sup>2</sup>

**Pentachromium Dicarbide,  $\text{Cr}_5\text{C}_2$ ,** can be prepared in quantity<sup>2</sup> by melting a mixture of chromium and a finely powdered chromium-carbon alloy containing 11.16 per cent. of carbon in a magnesia crucible at  $1800^\circ$  to  $1850^\circ$  C. After repeatedly washing the product with 2N hydrochloric acid until no more chromium dissolves, the carbide,  $\text{Cr}_5\text{C}_2$ , is obtained practically pure. It forms silvery crystals, of density 6.915 at  $24.8^\circ$  C. It is not attacked by aqua regia, and melts without appreciable decomposition at  $1665^\circ$  C.

**Tetrachromium Dicarbide,  $\text{Cr}_4\text{C}_2$ .**—By melting chromium at temperatures above  $1840^\circ$  C. for fifteen minutes in a crucible of pure carbon, frequently stirring with a carbon rod, alloys saturated with carbon are obtained. These contain no free chromium, but only carbide and graphite. On washing with hot 24 per cent. hydrochloric acid part of the alloy dissolves, and the ratio of chromium to carbon dissolving indicates that the soluble carbide has the composition  $\text{Cr}_4\text{C}_2$ ,<sup>2</sup> but the existence of this has not been confirmed by isolation.

The residue, insoluble in the hot acid, contains graphite and **trichromium dicarbide,  $\text{Cr}_3\text{C}_2$ ,** which, by extraction of graphite, can be obtained from 99 to 99.5 per cent. pure. Moissan<sup>3</sup> obtained this carbide during the reduction of chromic oxide by carbon in the electric furnace; also by heating metallic chromium with a large excess of carbon in the crucible of an electric furnace for ten to fifteen minutes, using a current of 350 amperes under 70 volts; and by heating<sup>4</sup> a mixture of equal parts of chromic oxide and calcium carbide in the electric arc for five minutes, using 900 amperes under 45 volts. It is obtained as lustrous lamellæ, unctuous, darker in colour than the pentachromium carbide. It is resistant to all acids; fused potassium hydroxide has little action upon it, but it is easily destroyed by fused potassium nitrate. Its density at  $21.3^\circ$  C. is 6.683,<sup>5</sup> and it is hard enough to scratch quartz and topaz. It does not attack water either at ordinary temperatures or at the boiling-point. It is stable at high temperatures, but it appears to undergo partial decomposition into the tetrachromium dicarbide,  $\text{Cr}_4\text{C}_2$ , and carbon on melting at about  $1890 \pm 10^\circ$  C., the molten carbide readily reducing magnesia, alumina

<sup>1</sup> Deville and Debray, *Ann. Chim. Phys.*, 1859, [3], 56, 408.

<sup>2</sup> Ruff and Foehr, *Zeitsch. anorg. Chem.*, 1918 104, 27.

<sup>3</sup> Moissan, *Compt. rend.*, 1894, 119, 185.

<sup>4</sup> Moissan, *ibid.*, 1897, 125, 841.

<sup>5</sup> Ruff and Foehr, *loc. cit.*; Moissan gives a density of 5.62.

and zirconia. It is decomposed by chlorine at a red heat, forming chromic chloride and amorphous carbon.

**Chromium Tungsten Carbide,  $3\text{Cr}_3\text{C}_2\cdot\text{W}_2\text{C}$ ,** is formed<sup>1</sup> by heating a mixture of chromic oxide, tungstic acid, and carbon in a carbon crucible in the electric furnace for five minutes with a current of 400 amperes under 75 volts, and treating the product with warm hydrochloric acid, and then with concentrated ammonia solution; or by heating a mixture of chromium, tungsten, carbon, and copper in a carbon crucible, and dissolving the copper from the product by washing with nitric acid. The double carbide is obtained in small, hard, crystalline grains, of density 8.41 at 22° C.; it is not magnetic. It is attacked by chlorine at 400° C.; bromine acts only slowly at 500° C., while iodine at that temperature does not affect it. When heated in air it does not burn. It is not attacked by acids; fused potassium hydroxide or alkali carbonates react only slowly; fused alkali nitrates or potassium chlorate rapidly decompose it, giving a mixture of chromate and tungstate. When heated in hydrogen chloride, chromic chloride, tungsten chloride, hydrogen, and methane are formed.

**Chromous Carbonate,  $\text{CrCO}_3$ ,** is obtained as a grey amorphous precipitate by the action of an alkali carbonate on a solution of a chromous salt.<sup>2</sup> It is soluble in water charged with carbon dioxide. When heated, carbon dioxide is evolved, leaving a residue of chromium sesquioxide.

A series of **double carbonates** has been prepared by acting on chromous acetate, or tartrate, with alkali carbonates.<sup>3</sup>

**Ammonium Chromous Carbonate,  $(\text{NH}_4)_2\text{CO}_3\cdot\text{CrCO}_3\cdot\text{H}_2\text{O}$ ,** is deposited as a yellow crystalline powder when an ammoniacal solution of chromous acetate is acted upon, first by a current of carbon dioxide, and then by a stream of hydrogen. The salt is washed successively with dilute ammonia solution, alcohol, and finally ether, and then dried in a stream of hydrogen containing a little ammonia. It may also be prepared by boiling the ammoniacal solution of chromous acetate with a solution of sodium carbonate in an atmosphere of hydrogen. The salt is an energetic reducer. It gradually decomposes on exposure to air, giving blue chromic hydroxide; heated in the air or in hydrogen it yields green chromium sesquioxide. It is attacked by chlorine at red heat, giving chromic chloride; with hydrogen sulphide, the sulphide,  $\text{Cr}_2\text{S}_3$ , is obtained as a black crystalline powder. In absence of oxygen dilute mineral acids dissolve it, yielding blue solutions.

**Potassium Chromous Carbonate,  $\text{K}_2\text{CO}_3\cdot\text{CrCO}_3\cdot 3\text{H}_2\text{O}$ ,** formed when chromous acetate is treated with a 20 per cent. solution of potassium carbonate, yields yellow hexagonal crystals.

**Sodium Chromous Carbonate,  $\text{Na}_2\text{CO}_3\cdot\text{CrCO}_3\cdot 10\text{H}_2\text{O}$ ,** separates as a reddish-brown powder when moist chromous acetate is mixed with a solution of sodium carbonate in an atmosphere of carbon dioxide. It yields microscopic, tabular, lozenge-shaped crystals. If heated at 100° C. in a current of a dry inert gas, the *monohydrate*,  $\text{Na}_2\text{CO}_3\cdot\text{CrCO}_3\cdot\text{H}_2\text{O}$ , is obtained.

<sup>1</sup> Moissan and Kouznetzow, *Compt. rend.*, 1903, 137, 292.

<sup>2</sup> Moissan, *Ann. Chim. Phys.*, 1882, [5], 25, 414. See also Moberg, *J. prakt. Chem.*, 1848, 44, 328.

<sup>3</sup> Beaugé, *Compt. rend.*, 1896, 122, 474; 1897, 125, 1177; 1898, 126, 1566; 1904, 38, 1219; *Bull. Soc. chim.*, 1898, [3], 19, 107; 1904, 31, 782; *Ann. Chim. Phys.*, 1900, 19, 158.

A red-brown *magnesium* compound has also been obtained. The carbonates of the alkaline earth metals have no action on chromous acetate.

**Chromic Carbonates.**—When a slight excess of an alkali carbonate is added to a solution of a chromic salt, a light greenish-blue precipitate falls, soluble, when freshly formed, in excess of the alkali carbonate or of borax.<sup>1</sup> The composition of the precipitate appears to vary with the conditions, the following compounds having been indicated:  $4\text{Cr}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$ ; <sup>2</sup>  $2\text{Cr}_2\text{O}_3 \cdot \text{CO}_2 \cdot 6\text{H}_2\text{O}$ ; <sup>3</sup>  $10\text{Cr}_2\text{O}_3 \cdot 7\text{CO}_2 \cdot 8\text{H}_2\text{O}$ ; <sup>4</sup>  $\text{Cr}_2\text{O}_3 \cdot \text{CO}_2 \cdot 4\text{H}_2\text{O}$ ; <sup>5</sup>  $\text{Cr}_2\text{O}_3 \cdot 2\text{CO}_2$ .<sup>6</sup> According to Lefort, the addition of an alkali carbonate to a solution of a green chromic salt precipitates chromic hydroxide, the carbonate only being deposited when violet salts are used; Parkmann maintains that both give the carbonate. The compound,  $\text{Cr}_2\text{O}_3 \cdot \text{CO}_2 \cdot 4\text{H}_2\text{O}$ , when heated to about  $75^\circ \text{C}$ ., loses 3 molecules of water, but the remaining molecule and carbon dioxide are only driven off at  $300^\circ \text{C}$ .<sup>7</sup>

When pure chromic hydroxide is exposed to the air, it absorbs carbon dioxide until the saturation limit is reached. Analysis of the compound obtained points to the formula  $[\text{Cr}_2(\text{OH})_5]_2\text{CO}_3 \cdot 8\text{H}_2\text{O}$ .<sup>8</sup> It can be dried at  $100^\circ \text{C}$ . without loss of  $\text{CO}_2$ , which, however, is liberated by acids.

**Chromium Thiocarbonate.**—When calcium thiocarbonate is added to a solution of a chromic salt, a grey-green precipitate resembling chromic hydroxide is produced, which on distillation yields carbon disulphide and a brown residue of chromium sesquisulphide,  $\text{Cr}_2\text{S}_3$ , which burns vividly in air, forming chromium sesquioxide.

## CHROMIUM AND CYANOGEN.

**Chromous Cyanide,  $\text{Cr}(\text{CN})_2$ ,** is obtained as a white precipitate when aqueous potassium cyanide is added to a solution of chromous chloride.<sup>9</sup> It is insoluble in excess of potassium cyanide, and is quickly oxidised in air to chromic cyanide and sesquioxide. It forms a series of double salts with metallic cyanides (see below).

**Chromic Cyanide,  $\text{Cr}(\text{CN})_3$ ,** is formed when a solution of potassium cyanide is added in excess to a neutral solution of chromic chloride and the mixture brought to boiling. It appears as a light greenish-blue precipitate, insoluble in excess of potassium cyanide. A similar reaction occurs with a solution of chrome alum, except that the mixture immediately turns green. The precipitate can be dried, in absence of air, without decomposition, as, for example, by heating in a stream of hydrogen at  $200^\circ \text{C}$ . It dissolves in boiling hydrochloric acid, giving a green solution, from which it is again precipitated by ammonia. Hot

<sup>1</sup> Heberling, *Chem. Zentr.*, 1870, 15, 122.

<sup>2</sup> Berzelius, *Lehrbuch der Chemie* (Dresden), 1848, 5th edn., 3, 1086.

<sup>3</sup> Langlois, *Ann. Chim. Phys.*, 1856, [3], 48, 502; *Jahresber.*, 1856, p. 551.

<sup>4</sup> Meissner, *Gilbert's Annalen*, 1818, 60, 366.

<sup>5</sup> Lefort, *Compt. rend.*, 1848, 27, 269; Wallace, *Chem. Gazette*, 1858, p. 410; *Jahresber.*, 1858, p. 71; Barratt, *Chem. News*, 1860, 1, 110; *Jahresber.*, 1860, p. 69.

<sup>6</sup> Parkmann, *Amer. J. Sci.*, 1862, [2], 34, 321; *Jahresber.*, 1862, p. 50.

<sup>7</sup> Lefort, *loc. cit.*

<sup>8</sup> Jovitschitsch, *Compt. rend.*, 1914, 158, 872.

<sup>9</sup> Berzelius, *Lehrbuch*, Leipzig, 1856. See also Rammelsberg, *Pogg. Annalen*, 1837, 42, 141.

potassium hydroxide decomposes it, with formation of chromic hydroxide and potassium chromicyanide <sup>1</sup> (see below).

**Potassium Chromocyanide**,  $K_4Cr(CN)_6$ , can be obtained pure by the addition of alcohol to a solution of chromous acetate in concentrated potassium cyanide solution,<sup>2</sup> or by shaking up chromous acetate with aqueous carbon dioxide, pouring the mixture into a 25 per cent. solution of potassium cyanide, the whole then being gently warmed in an atmosphere of hydrogen, cooled in snow, and precipitated by adding solid potassium cyanide.<sup>3</sup> The salt appears in the form of dark blue crystals, which are readily oxidised to the yellow chromicyanide—a fact which caused Moissan <sup>4</sup> to mistake the latter salt for the chromocyanide. Salts of the following metals, barium, iron ( $Fe^{++}$ ), lead, mercury ( $Hg^{++}$ ), and zinc, when added to a solution of potassium chromocyanide, produce <sup>2</sup> characteristically coloured precipitates.

**Hydrogen Chromicyanide, Chromicyanic Acid**,  $H_3[Cr(CN)_6]$ , is prepared by adding tartaric acid to a solution of potassium chromicyanide, or by passing hydrogen sulphide into water in which silver or lead chromicyanide is suspended.<sup>5</sup> In the latter case the insoluble sulphide is filtered off and the filtrate evaporated *in vacuo*. Reddish-yellow vitreous crystals are obtained which have an acid reaction. The aqueous solution on standing loses hydrogen cyanide, a change which also takes place on prolonged boiling of a solution of the acid in boiling hydrochloric acid, when the red liquid gradually becomes green, compounds of composition  $HCN.Cr(CN)_3$  and  $2HCN.Cr(CN)_3$  probably being formed.<sup>5</sup> Chromicyanic acid is tribasic, and forms salts analogous in composition to the ferriyanides.<sup>6</sup>

**Ammonium Chromicyanide**,  $(NH_4)_3[Cr(CN)_6]$ , has been obtained <sup>7</sup> by digesting the basic lead salt (see below) with excess of ammonium carbonate, and evaporating the liquid first by heating and then over sulphuric acid. The crystals, which belong to the monoclinic system,

$$a : b : c = 0.806 : 1 : 0.66 ; \beta = 72^\circ 14',$$

are isomorphous with the potassium salt and with potassium ferri-cyanide.

**Lithium Chromicyanide**,  $Li_3[Cr(CN)_6].5H_2O$ , is obtained <sup>8</sup> by passing hydrogen sulphide into an alcoholic solution containing equivalent quantities of lithium carbonate and silver chromicyanide; after expelling excess of hydrogen sulphide, adding a little water, and evaporating *in vacuo*, the salt crystallises in long needles.

**Sodium Chromicyanide**,<sup>8</sup>  $Na_3[Cr(CN)_6].5H_2O$  or  $8H_2O$ , crystallises only with difficulty. It may be prepared by the methods described below for the potassium salt, but the yellowish solution obtained yields a reddish-brown oil on evaporation, from which, with care, the pentahydrate may be obtained in small prisms. Needle-shaped crystals containing  $8H_2O$  have also been obtained.

**Potassium Chromicyanide**,  $K_3[Cr(CN)_6]$ , is the most important

<sup>1</sup> Berzelius, *Jahresber.*, 1843, 25, 307.

<sup>2</sup> Descamps, *Ann. Chim. Phys.*, 1881, [5], 24, 196.

<sup>3</sup> Christensen, *J. prakt. Chem.*, 1885, [2], 31, 163.

<sup>4</sup> Moissan, *Compt. rend.*, 1881, 93, 1079.

<sup>5</sup> Kaiser, *Annalen Suppl.*, 1864, 3, 171.

<sup>6</sup> Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 75.

<sup>7</sup> Kaiser, *loc. cit.*; Rölcke, *Dissertation*, Berlin, 1896.

<sup>8</sup> Rölcke, *loc. cit.*

salt of chromicyanic acid. It has been prepared by dissolving chromic hydroxide in an aqueous solution of potassium hydroxide which is supersaturated with hydrogen cyanide, and exposing the resulting liquid to air, when it assumes a reddish-brown colour and deposits crystals which may be purified by recrystallisation;<sup>1</sup> by adding excess of aqueous potassium cyanide to a solution of chromous acetate contained in a closed vessel, and allowing to stand for a week, when long yellow needles separate;<sup>2</sup> by the action of excess of potassium cyanide on chromous chloride or carbonate, or by heating powdered chromium with a concentrated solution of potassium cyanide in a sealed tube at 100° C.<sup>2</sup> However, it is best prepared<sup>3</sup> by the following method: Freshly precipitated moist chromic hydroxide is dissolved in acetic acid, and the solution evaporated nearly to dryness and then diluted considerably with water. This solution is gradually added to a hot solution of potassium cyanide (about 25 per cent.) contained in a flask so as to exclude atmospheric carbon dioxide. After heating for a short time the liquid is filtered, evaporated, and cooled. The crystals obtained are dissolved in water (4 parts) and the solution boiled. Chromic hydroxide is deposited and filtered off, and the filtrate on cooling deposits pale yellow crystals, more of which are obtained by repeatedly boiling the mother-liquor.

Potassium chromicyanide forms yellow, macled crystals, stable in air at ordinary temperatures; density 1.71. At 20° C., 1 c.c. of water dissolves 0.3233 gram of the salt.<sup>2</sup> The aqueous solution on prolonged boiling deposits chromium sesquioxide, with slight evolution of hydrogen cyanide. Heated to dull redness in absence of air, the solid fuses and then undergoes decomposition, giving off nitrogen and leaving chromium carbide and potassium cyanide. With dilute sulphuric acid hydrogen cyanide is evolved, while the concentrated acid liberates carbon monoxide.

When an aqueous solution of potassium chromicyanide is heated with carbon monoxide at 130° C. in a sealed tube, no absorption of the carbon monoxide takes place, but the chromicyanide is completely decomposed with the production of chromium sesquioxide, formic acid, hydrogen cyanide, and ammonia.<sup>4</sup>

The following insoluble chromicyanides are obtained as characteristically coloured precipitates when potassium chromicyanide is added to solutions of metallic salts.<sup>5</sup>

**Cadmium Chromicyanide**,  $\text{Cd}_3[\text{Cr}(\text{CN})_6]_2$ ; white, with a slight green tinge.

**Chromous Chromicyanide**,  $\text{Cr}_3[\text{Cr}(\text{CN})_6]_2$ ; dark coloured, almost black.

**Cobaltous Chromicyanide**,  $\text{Co}_3[\text{Cr}(\text{CN})_6]_2 \cdot 15\text{H}_2\text{O}$ ; light rose coloured, becoming yellowish brown on drying.

**Cuprous Chromicyanide**,  $\text{Cu}_3[\text{Cr}(\text{CN})_6]_2$ ; orange yellow.

**Cupric Chromicyanide**,  $\text{Cu}_3[\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ ; blue when first precipitated, gradually becomes green, and when dry reddish purple.

<sup>1</sup> Böckmann, see Gmelin's *Handbuch der Chemie*, 1848, 4, 335.

<sup>2</sup> Moissan, *Compt. rend.*, 1881, 93, 1079.

<sup>3</sup> Christensen, *J. prakt. Chem.*, 1885, [2], 31, 163.

<sup>4</sup> Müller, *Bull. Soc. chim.*, 1903, [3], 29, 27.

<sup>5</sup> van Dyke, Cruser, and Miller, *J. Amer. Chem. Soc.*, 1906, 28, 1132; Röcke, *loc. cit.*; Moissan, *loc. cit.*; Kaiser, *loc. cit.*



**Ferrous Chromicyanide**,  $\text{Fe}_3[\text{Cr}(\text{CN})_6]_2$ ; brick red, changing to dark green on drying.

**Lead Chromicyanide**,  $\text{Pb}_3[\text{Cr}(\text{CN})_6]_2 \cdot 30\text{H}_2\text{O}$ , is precipitated on the addition of alcohol to a solution of the basic salt in a limited quantity of dilute sulphuric acid. No precipitate is formed when potassium chromicyanide is added to a solution of lead nitrate, but the basic acetate of lead yields a white precipitate.<sup>1</sup>

The *basic* compound,  $\text{Pb}_3[\text{Cr}(\text{CN})_6]_2 \cdot 5\text{PbO}$ , is obtained as a yellowish-white amorphous precipitate on adding ammoniacal lead acetate solution to a dilute solution of potassium chromicyanide in absence of carbon dioxide.

**Manganous Chromicyanide**,  $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2$ ; greenish-white crystals; light brown when dry.

**Mercury Chromicyanide**.—The addition of potassium chromicyanide to a solution of mercurous nitrate gives a yellowish-white precipitate, which rapidly darkens and finally becomes grey. The original precipitate is probably **mercurous chromicyanide**,  $\text{Hg}_3[\text{Cr}(\text{CN})_6]$ , which decomposes, yielding mercurous cyanide, which in its turn splits up into mercuric cyanide and mercury.

**Nickel Chromicyanide**,  $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ ; light greenish blue; black when dry.

**Silver Chromicyanide**,  $\text{Ag}_3[\text{Cr}(\text{CN})_6]$ ; orange yellow; when dry rose red. It is decomposed by heat, yielding cyanogen and metallic silver.<sup>1</sup>

**Zinc Chromicyanide**,  $\text{Zn}_3[\text{Cr}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$ ; yellowish-white crystals; straw coloured when dry.

The behaviour of the above salts with mineral acids and with alkalis has been studied.<sup>2</sup>

**Chromium Oxycyanide**,  $\text{CrO}_2(\text{CN})_2$ .—The existence of this compound has been indicated,<sup>3</sup> but it has not yet been isolated.

**Chromous Thiocyanate**,  $\text{Cr}(\text{SCN})_2$ , and **Chromous Sodium Thiocyanate**,  $3\text{NaCNS} \cdot \text{Cr}(\text{CNS})_2 \cdot 11\text{H}_2\text{O}$ , are known to exist.<sup>4</sup> By passing nitric oxide into a moist amyl-alcoholic solution of chromous thiocyanate, the compound  $\text{O}[\text{Cr}(\text{SCN})_2]_2 \cdot 4\text{NH}_3$  is obtained.<sup>5</sup> Compounds with pyridine have also been described.

**Chromic Thiocyanate**,  $\text{Cr}(\text{SCN})_3$ , is prepared by dissolving freshly precipitated chromic hydroxide in thiocyanic acid and evaporating the green-violet solution over sulphuric acid,<sup>6</sup> or by concentrating a solution of chromithiocyanic acid (see below) either by heating or over sulphuric acid.<sup>7</sup> It is obtained as a grey, amorphous, deliquescent mass, which readily dissolves in water to form a violet solution. When freshly prepared, the solution does not answer to the ordinary precipitation reactions for the  $\text{Cr}'''$  and  $\text{SCN}'$  ions. However, hydrolytic dissociation gradually takes place, especially under the influence of sunlight; the solution becomes green, and precipitates are obtained with silver nitrate and ammonia solutions.<sup>8</sup> It is soluble in the chief organic solvents.

<sup>1</sup> Böckmann, *loc. cit.*

<sup>2</sup> van Dyke, Cruser, and Miller, *loc. cit.*

<sup>3</sup> Rawson, *Chem. News*, 1889, 59, 184.

<sup>4</sup> Koppel, *Zeitsch. anorg. Chem.*, 1905, 45, 359; Sand and Burger, *Ber.*, 1906, 39, 1771.

<sup>5</sup> Sand and Burger, *loc. cit.*

<sup>6</sup> Clasen, *Zeitsch. Chem.*, 1866, p. 102; *J. prakt. Chem.*, 1865, 96, 351; Graham Otto, *Anorg. Chem.*, 5th edn., 1881, 2, 1105.

<sup>7</sup> Rosler, *Annalen*, 1867, 141, 195.

<sup>8</sup> Speransky, *J. Russ. Phys. Chem. Soc.*, 1896, 28, [1], 329.

Ammoniated compounds, of composition  $\text{Cr}(\text{NH}_3)_2(\text{SCN})_3 \cdot \text{H}_2\text{O}$ ;  $\text{Cr}(\text{NH}_3)_2(\text{SCN})_3 \cdot 2\text{H}_2\text{O}$ ;  $\text{NH}_4\text{CNS} \cdot \text{Cr}(\text{NH}_3)_2(\text{SCN})_3$ ;  $\text{NH}_4\text{CNS} \cdot \text{Cr}(\text{NH}_3)_4(\text{SCN})_3$ ;  $\text{Cr}(\text{NH}_3)_2(\text{SCN})_4 \cdot \text{NH}_4\text{I}$ , have been prepared.<sup>1</sup>

Thiocyano salts of chromium with organic bases, *e.g.* pyridine and ethylenediamine, have also been obtained.<sup>2</sup>

**Chromithiocyanic Acid**,  $\text{H}_3[\text{Cr}(\text{SCN})_6]$ , is formed in the deep wine-red solution which results from the decomposition of the lead or silver salt of this acid.<sup>3</sup> The solution is strongly acid, but the compound has not been isolated, since on heating the solution gives off thiocyanic acid, and chromium thiocyanate remains behind. It forms salts containing the complex ion  $[\text{Cr}(\text{SCN})_6]'''$ , whose solutions, however, on long standing, especially under the influence of light, undergo ionic dissociation, as shown by freezing-point and conductivity determinations, and the resulting chemical activity.<sup>4</sup> The salts of the heavy metals are of characteristic colours.<sup>3</sup> The absorption spectra of some chromithiocyanates have been studied.<sup>5</sup>

**Ammonium Chromithiocyanate**,  $(\text{NH}_4)_3[\text{Cr}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$ , is formed by dissolving freshly precipitated hydroxide in ammoniumthiocyanate solution, or by reducing ammonium dichromate with alcohol and sulphuric acid, neutralising the solution with ammonia, adding ammonium thiocyanate, and boiling for a short time.<sup>6</sup>

**Sodium Chromithiocyanate**,  $\text{Na}_3[\text{Cr}(\text{SCN})_6] \cdot 12\text{H}_2\text{O}$ , yields crimson-coloured crystals, which over sulphuric acid, or when heated at  $105^\circ \text{C}$ ., become anhydrous and turn violet. A heptahydrate may be obtained by crystallisation from aqueous alcohol.

**Potassium Chromithiocyanate**,  $\text{K}_3[\text{Cr}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$ , prepared by boiling a solution of a chromic salt with potassium thiocyanate, forms reddish-violet glistening crystals, of density 1.71 at  $16^\circ \text{C}$ .<sup>7</sup> The salt is stable in the air and over sulphuric acid, but when heated to  $110^\circ \text{C}$ . it loses its water of crystallisation, and at higher temperatures decomposes. It dissolves in water, 1 part in 0.72 parts of water, yielding a red solution, which on boiling goes green, but on cooling returns to its original colour. By crystallising from aqueous alcohol a trihydrate may be obtained.

**Barium Chromithiocyanate**,  $\text{Ba}_3[\text{Cr}(\text{SCN})_6]_2 \cdot 16\text{H}_2\text{O}$ , is soluble in water, and is obtained by the methods employed for the alkali salts. It crystallises in short ruby-red prisms.

**Silver Chromithiocyanate**,  $\text{Ag}_3[\text{Cr}(\text{SCN})_6]$ , is obtained as a voluminous reddish-brown precipitate, which when boiled with water turns pink. It is insoluble in ammonia, and is not sensitive to light.

**Lead Chromithiocyanate**.—The normal salt has not been obtained. The addition of the potassium salt to a solution of lead acetate gives a

<sup>1</sup> See Morland, *Quart. J. Chem. Soc.*, 1860, 13, 252; Christensen, *J. prakt. Chem.*, 1892, [2], 45, 221; Nordenskjöld, *Zeitsch. anorg. Chem.*, 1892, 1, 135; Pfeiffer and Tingler, *ibid.*, 1908, 58, 433. See also Pfeiffer and Haimann, *Ber.*, 1903, 36, 1063; Escales and Ehrensperger, *ibid.*, 1903, 36, 2681; Werner and von Halban, *ibid.*, 1906, 39, 2668; Maas and Sand, *ibid.*, 1908, 41, 3367.

<sup>2</sup> Pfeiffer, *Ber.*, 1901, 34, 4303; Pfeiffer and Osann, *ibid.*, 1906, 39, 2115.

<sup>3</sup> Rosler, *loc. cit.*

<sup>4</sup> Magnanini, *Gazzetta*, 1895, 25, [2], 373; Speransky, *loc. cit.*; Cioci, *Zeitsch. anorg. Chem.*, 1899, 19, 314; Rosenheim and Cohn, *ibid.*, 1901, 27, 293.

<sup>5</sup> Magnanini, *loc. cit.*

<sup>6</sup> Rosler, *Annalen*, 1867, 141, 189.

<sup>7</sup> Clarke, *Amer. J. Sci.*, 1877, [3], 14, 281.

red precipitate, which when dried over sulphuric acid has the composition  $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2 \cdot 4\text{PbO} \cdot 12\text{H}_2\text{O}$ . This, with water, becomes yellow, and forms the compound  $\text{Pb}_2[\text{Cr}_2(\text{SCN})_{10}] \cdot 4\text{PbO} \cdot 9\text{H}_2\text{O}$ .<sup>1</sup>

**Chromium Ferrocyanide**,  $\text{Cr}_2[\text{Fe}(\text{CN})_6]$ , is obtained as a yellow precipitate when chromous chloride is added to a solution of potassium ferrocyanide.<sup>2</sup>

#### CHROMIUM AND SILICON.

Alloys of chromium and silicon are readily obtained by heating chromium sesquioxide with excess of silicon at full white heat,<sup>3</sup> or silicon carbide,<sup>4</sup> or silicon carbide and carbon,<sup>5</sup> in the electric furnace or by strongly heating chromium sesquioxide, silica, and aluminium. From these alloys several definite silicides have been isolated, which are usually grey in colour, hard and brittle, and very resistant to acids except hydrofluoric acid, which readily decomposes them. The silicides  $\text{Cr}_3\text{Si}$ ,  $\text{Cr}_2\text{Si}$ ,  $\text{Cr}_3\text{Si}_2$ , and  $\text{CrSi}_2$ , have been obtained in a state of comparative purity by special methods of preparation.<sup>7</sup>

**Trichromium Silicide**,  $\text{Cr}_3\text{Si}$ , has been prepared by heating a mixture containing 140 parts each of copper and aluminium with parts of chromium sesquioxide in a fireclay crucible;<sup>8</sup> on adding a small quantity of aluminium filings an energetic action occurs, and on cooling, a metallic ingot is obtained containing crystals of the silicide which can be separated from the metal by treating with aqua regia and then washing with water. It has also been obtained<sup>9</sup> by fusing a mixture of copper and chromium with a relatively small quantity of silicon in an electric furnace, and digesting the resulting button with nitric acid. It forms grey, prismatic, arborescent crystals, of density 6.52 at 18° C.,<sup>8</sup> hard enough to scratch glass, but not quartz. Acids have no action on it, except hydrofluoric acid; it is only slightly attacked by sulphur, potassium chlorate, or fused potash; chlorine and bromine decompose it at red heat, and it is rapidly attacked by a mixture of potassium chlorate and nitric acid.

**Dichromium Silicide**,  $\text{Cr}_2\text{Si}$ , has been prepared in the form of lozenge-shaped crystals with brilliant facets, by causing silicon to increase in proportions to act upon chromium dissolved in copper. Moissan<sup>10</sup> obtained it as small prismatic crystals by heating chromium in a dish lined with silicon at a temperature rather above 1200° C. in a current of hydrogen; by heating pure chromium with 15 per cent of silicon in a carbon crucible in an electric furnace; and by heating a mixture of 6 parts of silica, 20 parts of chromium sesquioxide and 7 parts of sugar carbon in the electric furnace. The product, which always contained some carbide, was washed with cold concentrated hydrofluoric acid. The crystals are hard enough to scratch quartz.

<sup>1</sup> Rosler, *Annalen*, 1867, 141, 189.

<sup>2</sup> Stridsberg, *Jahresber.*, 1864, p. 304; Kaiser, *Annalen Suppl.*, 1864, 3, 163.

<sup>3</sup> Warren, *Chem. News*, 1898, 78, 318.

<sup>4</sup> Frilley, *Revue Métallurgie*, 1911, 8, 476.

<sup>5</sup> Baraduc-Muller, *ibid.*, 1909, 6, 157; 1910, 7, 698.

<sup>6</sup> Matignon and Trannoy, *Compt. rend.*, 1905, 141, 190.

<sup>7</sup> For a general study of the alloys of chromium and silicon, see Frilley, *loc. cit.*

<sup>8</sup> Zettel, *Compt. rend.*, 1898, 126, 833.

<sup>9</sup> Lebeau and Figueras, *Bull. Soc. chim.*, 1903, [3], 29, 799.

<sup>10</sup> Moissan, *Compt. rend.*, 1895, 121, 621.

even corundum. The silicide is attacked at red heat by chlorine with incandescence; hydrogen chloride at 700° C. gives the chlorides of silicon and chromium; fused potash slowly attacks it.

**Trichromium Disilicide,  $\text{Cr}_3\text{Si}_2$ ,** is obtained by fusing a mixture of copper silicide with 4 per cent. of its weight of chromium in an electric furnace, and digesting the resulting mass alternately with 50 per cent. nitric acid and 10 per cent. caustic soda solution.<sup>1</sup> It has also been prepared by prolonged heating at 1200° C. of pure chromium powder in contact with silicon tetrachloride.<sup>2</sup> It yields long quadratic prisms, of density 5.6 at 0° C. It is hard enough to scratch glass, but not quartz. It is stable in air at ordinary temperatures, but is oxidised superficially at 1100° C. It becomes incandescent in chlorine at 400° C., and forms silicon and chromic chlorides; bromine attacks it slowly at red heat. It is not attacked by sulphuric or nitric acids; warm concentrated hydrochloric acid, or gaseous hydrogen chloride, gives chromous chloride; hydrofluoric acid also decomposes it. When fused with alkali carbonates, the alkali silicate and chromium sesquioxide are produced.

**Chromium Disilicide,  $\text{CrSi}_2$ ,** has been prepared by the method described for the previous compound, a higher percentage of silicon being used.<sup>3</sup> It has also been obtained<sup>4</sup> by heating a mixture of chromium sesquioxide and charcoal with excess of silica in an electric furnace. By the first method the silicide is obtained as a grey crystalline powder; by the second, as long, grey, lustrous needles, only obtained free from silicon with difficulty. Density 4.393.<sup>4</sup> It is decomposed by hydrofluoric acid.

**Chromium Aluminium Silicide,  $\text{Cr}_2\text{AlSi}_3$ ,** has been obtained<sup>5</sup> by fusing together silicon, aluminium, and chromium in an atmosphere of hydrogen in a reverberatory furnace; by the reduction of the powdered silicate of aluminium and chromium, or of a mixture of the oxide with silica by the thermit process; and by heating chromium, chromium sesquioxide, chromium sesquisulphide, potassium dichromate or potassium chromi fluoride,<sup>6</sup> with a large excess of potassium silicofluoride and aluminium in a Perrot's furnace, and dissolving away the regulus by alternate treatment with dilute hydrochloric acid and sodium hydroxide solution. The double silicide is obtained in the form of greyish-white, brittle, hexagonal crystals, which have a metallic lustre and conduct electricity. Its hardness is 4.7; density 5. It is insoluble in acids, except hydrofluoric acid, and in aqueous alkalis, but dissolves readily in molten sodium hydroxide. It is attacked by the halogens at high temperatures.

If in the method of preparation last described the proportions are so chosen that the regulus contains 35 to 50 per cent. of free silicon, then a second silicide,  $\text{Cr}_2\text{AlSi}_4$ , is formed,<sup>6</sup> yielding small crystals of hardness rather less than 5, and of density 4.8.

Manchot and Kieser<sup>7</sup> have studied the reaction of these silicides

<sup>1</sup> Lebeau and Figueras, *Compt. rend.*, 1903, 136, 1329; *Bull. Soc. chim.*, 1903, [3], 29, 799.

<sup>2</sup> Vigouroux, *Compt. rend.*, 1907, 144, 83.

<sup>3</sup> Lebeau and Figueras, *loc. cit.*

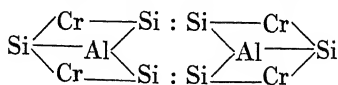
<sup>4</sup> De Chalmot, *Amer. Chem. J.*, 1897, 19, 69.

<sup>5</sup> Vigouroux, *Compt. rend.*, 1905, 141, 952; *Bull. Soc. chim.*, 1907, [4], 1, 790.

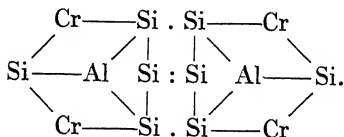
<sup>6</sup> Manchot and Kieser, *Annalen*, 1904, 337, 353.

<sup>7</sup> Manchot and Kieser, *ibid.*, 1905, 342, 356.

with hydrofluoric acid quantitatively, with the object of arriving at their constitution. They suggest the double formulæ:



and



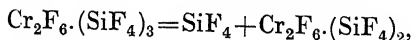
**Silicates** of chromium have not been prepared. Numerous siliceous minerals contain chromium sesquioxide, generally in combination with the oxides of aluminium and iron, *e.g.* chrome ochre and wolchonskoite (see p. 8).

A number of complex silicates of sodium and chromium have been prepared:

**Sodium Chromisilicates.**—By fusing together silica, sodium carbonate, and chromium sesquioxide with a large excess of sodium chloride, dark green orthorhombic and strongly pleochroic crystals, of composition  $2\text{Na}_2\text{O} \cdot 3\text{Cr}_2\text{O}_3 \cdot 6\text{SiO}_2$ , have been obtained.<sup>1</sup> From a mixture of sodium metasilicate, chromic hydroxide, and excess of sodium chloride, rhombic crystals, of composition  $5\text{Na}_2\text{O} \cdot 2\text{Cr}_2\text{O}_3 \cdot 11\text{SiO}_2$ , resulted; while a mixture of ammonium dichromate, sodium metasilicate, and sodium chloride yielded crystals resembling tridymite, of composition  $3\text{Na}_2\text{O} \cdot 2\text{Cr}_2\text{O}_3 \cdot 95\text{SiO}_2$ . When the sodium salts were replaced by salts of other alkali metals or of the alkaline earth metals, analogous compounds were not obtained. A sodium chromisilicate, of composition  $\text{Na}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 2\text{SiO}_2 + (?)\text{H}_2\text{O}$ , has also been described.<sup>2</sup> Chromultramarine is a soft, light green powder, of composition  $\text{Na}_2\text{O}(\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3)2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ , which, when boiled with sodium sulphide, gives ultramarine green.<sup>3</sup>

Compounds, of composition  $4(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \cdot \text{Na}_2\text{CrO}_4 \cdot 5\text{H}_2\text{O}$ <sup>4</sup> and  $5\text{Na}_2\text{O} \cdot 4\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 \cdot \text{CrO}_3$ ,<sup>5</sup> have been obtained by heating a mixture of kaolin and sodium chromate with sodium hydroxide or carbonate.

**Chromium Silicofluoride**,  $\text{Cr}_2\text{F}_6 \cdot (\text{SiF}_4)_3$ , is obtained in solution when chromium sesquioxide is dissolved in hydrofluosilicic acid.<sup>6</sup> It has not yet been isolated, since in aqueous solution it undergoes decomposition; the violet solution spontaneously and gradually becomes bluish green, and silicon tetrafluoride is liberated, thus: <sup>7</sup>



the silicon tetrafluoride then being decomposed by water. On evaporation more silicon tetrafluoride is liberated, and a green hydrated fluoride can be isolated,<sup>8</sup> to which Recoura gives the formula  $(\text{CrF}_3 \cdot 5\text{H}_2\text{O})\text{SiF}_6$ ,

<sup>1</sup> Weyberg, *Centr. Min.*, 1908, p. 519.

<sup>2</sup> Singer, *Dissertation, Technische Hochschule* (Berlin), 1910, p. 36.

<sup>3</sup> Singer, *German Patent*, 221344 (1909).

<sup>4</sup> Thugutt, *Zeitsch. anorg. Chem.*, 1892, 2, 85.

<sup>5</sup> Weyberg, *Centr. Min.*, 1904, p. 727.

<sup>6</sup> Berzelius, *Pogg. Annalen*, 1824, 1, 201.

<sup>7</sup> Recoura, *Compt. rend.*, 1913, 156, 1618.

<sup>8</sup> Recoura, *ibid.*, 1913, 157, 1525.

considering it analogous to the two silicofluorides prepared by Jørgensen,<sup>1</sup> of composition  $(\text{CrCl}_5\text{NH}_3)\text{SiF}_6$  and  $(\text{CrCl}_4\text{NH}_3\cdot\text{H}_2\text{O})\text{SiF}_6$ .

The freshly prepared violet solution of chromium silicofluoride reacts with potassium chloride, thus :



but if the solution has been allowed to stand, the products are potassium silicofluoride and a compound,  $(\text{Cr}_2\text{F}_2)\text{Cl}_4$ , from which the fluorine cannot be precipitated by adding barium chloride.

The *hydrated* compound  $(\text{CrF}_5\text{H}_2\text{O})\text{SiF}_6$  is stable in dry air or in a vacuum; but in contact with moist air it slowly loses silicon tetrafluoride, and ultimately yields hydrated chromic fluoride,  $\text{Cr}_2\text{F}_6\cdot 7\text{H}_2\text{O}$ .

### CHROMIUM AND BORON.

When chromium, or chromium sesquioxide, is heated with boron in an electric furnace, borides are formed.<sup>2</sup> If the operation is carried out in a carbon crucible, the product always contains free carbon which cannot be completely separated. By reducing the sesquioxide by heating with boron in magnesia crucibles in an electric furnace, du Jassonneix<sup>3</sup> obtained a series of alloys containing 5 to 17 per cent. of combined boron, and succeeded in isolating two definite borides of composition  $\text{CrB}$  and  $\text{Cr}_3\text{B}_2$ .

**Chromium Boride,  $\text{CrB}$ ,** was extracted from an alloy containing 16 per cent. of boron by the action of hydrochloric acid or chlorine below red heat. It contains 17.4 per cent. of boron, and represents the limit of saturation of chromium by boron. It is non-crystalline, of density 6.1 at 15° C., and hard enough to scratch glass or quartz. It is attacked by hydrochloric, hydrofluoric, or sulphuric acid, yielding boric acid; nitric acid and alkaline solutions have no action upon it; chlorine decomposes it with incandescence, forming chromous and chromic chlorides; hydrochloric acid acts similarly at red heat, evolving hydrogen; fused alkalis cause oxidation with incandescence. It burns spontaneously in fluorine, and, when heated to a white heat in nitrogen, it yields a greyish-black substance which, with fused potassium hydroxide, gives off ammonia.

A boride of very different properties, but to which the same composition is assigned, has been obtained<sup>4</sup> as a silver-white crystalline powder by the aluminothermic method, the chromium thermite being caused to react with boron, and excess of chromium being removed from the product by successively washing with dilute hydrochloric acid, nitric acid, and aqua regia. The pure boride had a density of 5.4 at 17° C., and hardness 8. It was unattacked by acids, even hydrofluoric acid, and only slightly attacked by fused sodium hydroxide, potassium nitrate, or potassium chlorate; sodium peroxide oxidised it with incandescence, forming borate and chromate. It possessed weak magnetic properties.

**Trichromium Diboride,  $\text{Cr}_3\text{B}_2$ ,** was isolated by Jassonneix<sup>5</sup>

<sup>1</sup> Jørgensen, *J. prakt. Chem.*, 1890, **42**, 206, 218.

<sup>2</sup> Tucker and Moody, *Proc. Chem. Soc.*, 1901, **17**, 129; *Trans. Chem. Soc.*, 1902, **81**, 14.

<sup>3</sup> du Jassonneix, *Compt. rend.*, 1906, **143**, 897, 1149; *Bull. Soc. chim.*, 1907, [4], **1**, 250.

<sup>4</sup> Wedekind and Fetzner, *Ber.*, 1907, **40**, 297; *Chem. Zeit.*, 1905, **29**, No. 98.

<sup>5</sup> du Jassonneix, *Compt. rend.*, 1906, **143**, 1149.

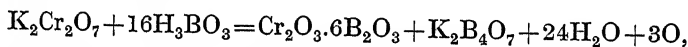
from an alloy containing 11.6 per cent. of boron. Its chemical properties closely resemble those of the monoboride prepared by this method, but in general it is not so readily attacked; for example, in fluorine it only takes fire when gently heated, and it is not attacked by nitrogen at white heat. Its density at 15° C. is 6.7.

**Chromous Borate.**—When a solution of borax, or of sodium metaborate, is added to aqueous chromous chloride, a pale blue amorphous precipitate is formed, which is soluble in free acids but insoluble in excess of the reagent.<sup>1</sup>

**Chromic Borate.**—Ammonium hydrogen metaborate,  $(\text{NH}_4)\text{HB}_2\text{O}_4$ , when added to a dilute solution of chromic chloride, causes the precipitation of a pale green powder.<sup>2</sup>

If borax is used the precipitate is blue, and is soluble in excess of the reagent;<sup>3</sup> with potassium hexaborate,  $\text{K}_2\text{O} \cdot 6\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ , the precipitate is green.<sup>4</sup> Hebbeling<sup>5</sup> gives the composition of the product as approximating to  $7\text{Cr}_2\text{O}_3 \cdot 4\text{B}_2\text{O}_3$ , but the proportion of  $\text{B}_2\text{O}_3$  present appears to vary with the concentration of the reagent.

**Guignet's Green** (see p. 37) is obtained by heating together potassium dichromate and boric acid and treating the fused product with water.<sup>6</sup> Salvétat<sup>7</sup> assumed that a chromiborate was formed according to the equation :



the chromiborate being decomposed by water with evolution of heat. A similar compound, usable as a dye, was obtained by Poussier<sup>8</sup> by heating chromium chloride with calcium borate.

#### DETECTION AND ESTIMATION OF CHROMIUM.

The distinctive colours of chromium compounds and their solutions render detection of the metal comparatively simple. The quantitative estimation of chromium is not difficult, and the principles of the more convenient and accurate methods are given in the following pages.<sup>9</sup>

**Detection: Dry Tests.**—Chromium compounds when reduced on charcoal leave a dark green residue; if the substance be first mixed with sodium carbonate, the fused mass obtained gives a yellow solution with water, the tint of which deepens on addition of sulphuric acid; in the presence of zinc, zinc chromate, which is insoluble in the alkaline solution, is formed.<sup>10</sup> On heating a chromate in a dry tube with a little potassium hydrogen sulphate, a red or green liquid may be formed with evolution of oxygen. Some chromates evolve oxygen when

<sup>1</sup> Moberg, *J. prakt. Chem.*, 1891, 44, 322.

<sup>2</sup> Hayes, *Amer. J. Sci.*, 1831, 20, 401.

<sup>3</sup> Berlin, see Gmelin's *Handbuch der Chemie*, 1850, 4, 122. See also Tissier, *Compt. rend.*, 1857, 45, 411; *Jahresber.*, 1857, p. 94.

<sup>4</sup> Laurent, Gmelin's *Handbuch der Chemie*, 1850, 4, 122.

<sup>5</sup> Hebbeling, *Chem. Zentr.*, 1870, p. 122; *Jahresber.*, 1870, p. 1001.

<sup>6</sup> Guignet, *Jahresber.*, 1859, p. 761.

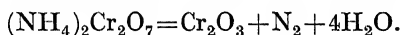
<sup>7</sup> Salvétat, *Compt. rend.*, 1859, 48, 295.

<sup>8</sup> Poussier, *Bull. Soc. chim.*, 1873, [2], 19, 334.

<sup>9</sup> For actual working details text-books of analysis must be consulted; for the analysis of chromium steels and ferrochrome the reader is referred to Vol. IX., Part III., of this series.

<sup>10</sup> Chancel, *Compt. rend.*, 1856, 43, 927.

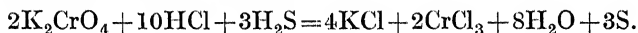
heated alone. Ammonium dichromate decomposes on heating, giving off nitrogen, while the sesquioxide is left as a bulky green powder,



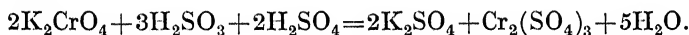
Some undecomposed ammonia also escapes.

If a trace of chromate or dichromate be heated in an opaque bead of fusion mixture on a platinum wire, a yellow bead results; a chromium salt will give the same result if the bead is touched with a minute quantity of sodium peroxide. When heated with borax on platinum wire in an oxidising flame, chromium compounds impart to the bead a yellow or dark red colour, which on cooling becomes yellowish green; if heated in the reducing flame an emerald green bead is obtained.

*Wet Tests.*—The presence of chromium in solution and its state of oxidation may be indicated by the colour due to its ions; thus  $\text{Cr}^{+++}$  is green,  $\text{CrO}_4^{--}$  yellow, and  $\text{Cr}_2\text{O}_7^{--}$  orange. The solutions of chromous salts are generally deep blue. When hydrogen sulphide is passed into a solution of chromate in presence of an acid, the colour changes to green and sulphur is precipitated:

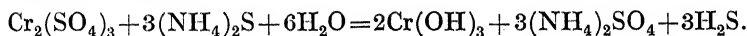


A similar change takes place with sulphurous acid, but no sulphur is precipitated:



If an excess of hydrogen peroxide be added to a solution containing a chromate, made slightly acid with sulphuric acid, and the mixture then shaken up with a few c.c. of ether, a blue ethereal layer is formed above the aqueous solution.<sup>1</sup> The colour is due to the formation of perchromic acid (see p. 73), and the reaction affords a useful test for identifying chromates in presence of sulphuric acid. If the ether used is free from alcohol, 1 part of potassium chromate in 40,000 parts of water can be detected. Another sensitive test for chromates and dichromates is to add a trace of  $\alpha$ -naphthylamine to the solution and acidify with tartaric acid, when an intense blue colour results.<sup>2</sup>

Solutions of chromic salts give a bluish- or whitish-green gelatinous precipitate of chromic hydroxide with ammonia, slightly soluble in excess of the reagent, forming a bluish-pink solution, but completely precipitated on boiling. Sodium or potassium hydroxide gives the same precipitate, which dissolves in excess of either reagent, giving a bright green solution; complete precipitation only takes place on prolonged boiling with a large excess of water. The presence of non-volatile organic compounds interferes with the precipitation and may entirely prevent it. Ammonium sulphide produces the same precipitate, insoluble in excess:



Chromium may also be precipitated as chromium phosphate,  $\text{CrPO}_4$  (see p. 87).

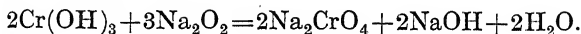
A chromium salt may be converted to a chromate by means of such oxidising agents as sodium peroxide, hydrogen peroxide, potassium per-

<sup>1</sup> Barreswill, *Ann. Chim. Phys.*, 1847, [3], 20, 364.

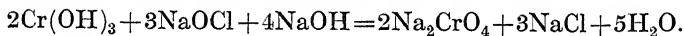
<sup>2</sup> van Eck, *Chem. Weekblad*, 1915, 12, 6.



sulphate, or an alkali hypochlorite or hypobromite. If sodium peroxide is used, it is added to a cold solution of the chromium salt, and the mixture then boiled until the effervescence ceases. The green or purple colour changes to yellow.



If the oxidation is carried out with a hypochlorite or hypobromite, chlorine or bromine water is added to a cold solution of the chromic salt, which has previously been rendered alkaline with sodium or potassium hydroxide, and the mixture is then boiled.



Excess of the halogen may be removed by acidifying with sulphuric acid and again boiling.

Since chromates and dichromates are powerful oxidisers, warming with concentrated hydrochloric acid results in the liberation of chlorine. In presence of a chloride these salts may be detected by heating with concentrated sulphuric acid, when chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , distils over as a greenish-yellow vapour, which condenses to a reddish-brown liquid (see p. 30).

When analysing a substance containing a chromate, the latter is reduced by hydrogen sulphide with precipitation of sulphur; it is therefore precipitated as hydroxide in the iron group. To avoid the sulphur precipitate, the reduction may be performed with sulphurous acid, excess being expelled by boiling before passing in hydrogen sulphide. The precipitated hydroxides of iron, aluminium, and chromium are treated with water and sodium peroxide, when the aluminium and chromium pass into solution as aluminate and chromate respectively. The presence of the latter is seen by the yellow colour, and can be confirmed by the precipitation of an insoluble chromate from the neutral or slightly acid solution. For example, silver nitrate gives a brick-red precipitate of silver chromate, insoluble in acetic acid but soluble in nitric acid and in ammonia; a soluble lead salt precipitates yellow lead chromate,<sup>1</sup> soluble in excess of caustic alkali; barium chloride gives light yellow barium chromate, soluble in mineral acids but insoluble in acetic acid; dark red mercurous chromate may also be precipitated.

To detect a chromium salt in the presence of a chromate, the mixture may be boiled with sodium carbonate and filtered; chromium hydroxide is precipitated from the chromium salt, while the yellow colour of the chromate is seen in the filtrate.

A chromate may be detected in presence of a dichromate in several ways. If the precipitation of barium chromate by excess of barium chloride leaves an acid solution, a dichromate is indicated. Excess of methylene blue gives a precipitate with dichromates, and if a chromate is present a further precipitate is obtained on adding dilute sulphuric acid to the filtrate. A concentrated solution of manganese sulphate added to a boiling solution gives a blackish-brown precipitate if a chromate is present; while by mixing the hot solution with an equal volume of a boiling solution of sodium thiosulphate, a distinct turbidity, or even a brown precipitate of chromium sesquioxide, is produced by a dichromate.

<sup>1</sup> Terreil, *Bull. Soc. chim.*, 1865, [2], 3, 30; *Chem. News*, 1865, 11, 136

Free chromic acid in a solution of a dichromate may be detected by the liberation of iodine from potassium iodide.

**Estimation of Chromium.**—In the analysis of chromites or of other substances containing chromium, such as leather ashes, pigments, etc., it is first necessary to obtain a solution. This is done by finely powdering the substance and heating it with a suitable flux in a crucible, preferably of nickel. Many fluxes have been employed, usually caustic alkali or alkali carbonates, but the one in most common use at present is sodium peroxide, whereby the chromium compound is rapidly converted to a chromate.<sup>1</sup> Excess of alkali is removed by boiling with ammonium carbonate, which also precipitates any iron present. The filtrate is then acidified with dilute sulphuric acid and the chromium estimated either by gravimetric or volumetric methods.

**Gravimetric Methods.**—When the chromium is in solution as a chromic salt, it can be precipitated completely from the boiling solution by the addition of ammonium hydroxide in the presence of ammonium salts.<sup>2</sup> The precipitate may be dried at 100° C. and converted by gentle ignition to the dark green sesquioxide and weighed as such. Ammonium sulphide<sup>3</sup> or hydrazine sulphate<sup>4</sup> may also be used as the precipitant.

The results obtained are generally high, probably due to the formation of chromic chromate during ignition,<sup>5</sup> thus :



Accurate results are obtained by igniting in hydrogen.

Chromium may also be completely precipitated as the phosphate,  $\text{CrPO}_4$ , by the addition of an alkali phosphate in presence of sodium acetate. The method gives satisfactory results with the green and violet chlorides, sulphates, and acetates, but not with oxalates (see p. 87).

If the chromium is in solution as a chromate or dichromate, as is the case after fusion as described above, it may either be reduced to the trivalent condition and precipitated as hydroxide, or directly precipitated as an insoluble chromate. In the absence of sulphates, barium chromate<sup>6</sup> is precipitated by the addition of barium acetate at the boiling-point to a solution made faintly acid with acetic acid and containing a little alcohol. After ignition the precipitate is weighed as barium chromate. If chlorides and sulphates are present only in small amount, the chromate may be thrown down by mercurous nitrate, the mercurous chromate then being converted by ignition to the sesqui-

<sup>1</sup> Hempel, *Zeitsch. anorg. Chem.*, 1893, 3, 193; Tompkins, *Chem. News*, 1893, 68, 136; Clark, *J. Chem. Soc.*, 1893, 63, 1079; Saniter, *J. Iron Steel Inst.*, 1895, 43, 153; *J. Soc. Chem. Ind.*, 1896, 15, 156; Rideal and Roseblum, *ibid.*, 1895, 14, 1017; Glaser, *J. Amer. Chem. Soc.*, 1898, 20, 130; *Chem. News*, 1898, 77, 123; Tate, *ibid.*, 1899, 80, 235; Fresenius and Bayerlein, *Zeitsch. anal. Chem.*, 1898, 37, 31. See also Levi and Orthmann, *Chem. Zentr.*, 1915, i., 219; Field, *J. Ind. Eng. Chem.*, 1916, 8, 238; Moir, *J.S. Ass. Anal. Chem.*, 1919, 2, [1], 9; *J. Soc. Chem. Ind.*, 1919, 38, 260 A.

<sup>2</sup> Jovitschitsch, *Monatsh.*, 1913, 34, 225.

<sup>3</sup> Hannus and Lucas, *Chem. Zeit.*, 1912, 36, 1134.

<sup>4</sup> Jannasch and Mai, *Ber.*, 1893, 26, 1786; Jannasch and Ruhl, *J. prakt. Chem.*, 1905, [2], 72, 10; Friedheim and Hasenclever, *Zeitsch. anal. Chem.*, 1905, 44, 594.

<sup>5</sup> Rothaug, *Zeitsch. anorg. Chem.*, 1913, 84, 165.

<sup>6</sup> Chancel, *Compt. rend.*, 1856, 43, 927; Gibbs, *Zeitsch. anal. Chem.*, 1893, 32, 309.

oxide of chromium. In the absence of chlorides the silver or lead salts may be precipitated, the latter only in absence of sulphates.<sup>1</sup>

*Volumetric Methods.*—Chromium is most easily estimated in solutions containing chromate or dichromate by volumetric methods.<sup>2</sup> These generally depend either on the oxidation of ferrous iron or on the liberation of iodine from potassium iodide.

In the first case, the solution is acidified with dilute sulphuric acid and a known excess of ferrous ammonium sulphate added. The excess of ferrous salt remaining in the solution is titrated with standard dichromate<sup>3</sup> or permanganate, the value of the original chromate solution being obtained from the amount of iron oxidised. The method gives exact results in the presence of iron, and it is used for the analysis of ferrochrome, steel, and slags,<sup>4</sup> but not in presence of nickel, cobalt, or manganese.<sup>5</sup> Similar methods are employed in the presence of aluminium, zinc, manganese, or vanadium, in which the chromium is oxidised by means of ammonium persulphate,<sup>6</sup> small quantities of chromium in steels and other metallurgical products being thus rapidly estimated.<sup>7</sup> The electrometric method for determining the end-point in the final titration of the ferrous iron has been used with success.<sup>8</sup>

The iodometric method depends on the fact that chromates interact with hydrochloric acid, liberating chlorine, which in its turn liberates an equivalent amount of iodine from potassium iodide. The iodine may then be determined by titration with standard sodium thio-sulphate. This method is largely used for chromium in whatever state of oxidation it may be, a chromium salt being first converted to chromate either by fusion with sodium peroxide<sup>9</sup> or by boiling its solution with nitric acid and lead dioxide.<sup>10</sup>

If iron is present results may be high, and this metal should therefore be removed by means of hydrogen peroxide before estimating the chromium; on the other hand, organic matter tends to delay the separation of iodine.<sup>11</sup> The reaction is also influenced by the concentration of the acid, the presence of different salts, and by sunlight.<sup>12</sup>

In chrome liquors, infusions, leather ashes, and chrome residues,

<sup>1</sup> Winkler, *Zeitsch. angew. Chem.*, 1918, 31, 46.

<sup>2</sup> On the estimation of chromic acid in solution, see Wallis, *Chemist and Druggist*, 1907, 71, 173.

<sup>3</sup> For the use of potassium dichromate as a volumetric standard, see Bruhns, *J. prakt. Chem.*, 1916, [2], 93, 73, 312; 1917, [2], 95, 37; M'Crosky, *J. Amer. Chem. Soc.*, 1918, 40, 1662.

<sup>4</sup> Koch, *Chem. Zeit.*, 1917, 41, 64; *Chem. Zentr.*, 1917, i., 532, 817; Herwig, *ibid.*, 1916, ii., 693; Schumacher, *ibid.*, 1917, i., 532.

<sup>5</sup> For a complete scheme for the analysis of nickel-iron-chromium alloys, see Reid, *J. Ind. Eng. Chem.*, 1917, 9, 488.

<sup>6</sup> van Felt, *Bull. de Belg.*, 1914, 28, 101, 138.

<sup>7</sup> Travers, *Compt. rend.*, 1917, 165, 187; Tusker, *Chem. Zeit.*, 1915, 39, 122; Daniels, *J. Ind. Eng. Chem.*, 1914, 6, 658.

<sup>8</sup> Kelley and Conant, *J. Ind. Eng. Chem.*, 1916, 8, 719; Kelley, Adams, and Wiley, *ibid.*, 1917, 9, 780; Edgar, *J. Amer. Chem. Soc.*, 1917, 39, 914.

<sup>9</sup> Field, *J. Ind. Eng. Chem.*, 1916, 8, 238.

<sup>10</sup> Terni and Malaguti, *Gazzetta*, 1919, 49, i., 251.

<sup>11</sup> Lauffmann, *Ledertechn. Rundschau*, 1918, 10, 37; *Chem. Zentr.*, 1918, ii., 310. Also Schorlemmer, *Collegium*, 1918, p. 145.

<sup>12</sup> Kolthoff and Vogelenzang, *Pharm. Weekblad*, 1919, 56, 514; Barnebey, *J. Amer. Chem. Soc.*, 1917, 39, 604.

the chromium is generally oxidised by one of the above methods and then estimated volumetrically.<sup>1</sup>

A method, which is considered sufficiently accurate for technical purposes, for the estimation of alkali chromates and dichromates in presence of each other, depends upon titration with acid or alkali.<sup>2</sup> Potassium dichromate is titrated with potassium hydroxide in presence of phenolphthalein :



The presence of an indicator is not essential, since when neutral the colour changes from reddish yellow to greenish yellow. Potassium chromate is estimated by titration with sulphuric acid, Congo red being used as the indicator :



A further method consists in treating a solution of chromate with an excess of methylene white (the leuco base of methylene blue) in presence of hydrochloric acid.<sup>3</sup> The methylene blue produced is then titrated with standard titanous chloride, the temperature being kept above 40° C. in order to sharpen the end-point.<sup>4</sup> The whole process should be performed in an atmosphere of carbon dioxide. In applying this method to ferrochrome or chromium steel, the iron and chromium may be estimated together, the iron then being determined separately by ordinary methods and the chromium obtained by difference. The reaction may also be used colorimetrically.<sup>5</sup>

*Colorimetric Methods.* The intensity of the yellow colour of a solution of an alkali chromate is proportional to the amount of chromate in the solution.<sup>6</sup> If, therefore, a given quantity of the solution to be tested has the same tint as an equal depth of a standard solution, it is assumed that there is the same concentration of alkali chromate in both solutions. The sensitiveness is found to be greatest at concentrations between 0.004N and 0.008N with respect to the gram-atom of chromium.<sup>7</sup>

Colorimetric comparisons have also been made with green chromium-chloride solutions, and it is found that, in general, the sensitiveness is similar to that of potassium chromate solutions.

When an alcoholic solution of diphenylcarbazide, containing a little acetic acid, is added to a very dilute solution of chromic acid, a violet coloration is produced. This has been made the basis of a colorimetric estimation.<sup>8</sup> With more concentrated solutions the reaction gives a reddish-brown colour, and finally a brown precipitate containing about 18 per cent. of chromium.

<sup>1</sup> Levi and Orthmann, *Chem. Zentr.*, 1915, i., 219; Schorlemmer, *ibid.*, 1918, i., 377; Appellins and Schmidt, *ibid.*, 1916, ii., 109.

<sup>2</sup> Sacher, *Farbenzeitung*, 1916, 22, 213; *Chem. Zentr.*, 1917, i., 693.

<sup>3</sup> Atack, *Analyst*, 1913, 38, 99; *J. Soc. Dyers and Colourists*, 1915, 31, 183, 203.

<sup>4</sup> The end-point is also sharpened by the presence of tartrates (Clark, *J. Washington Acad. Sci.*, 1920, 10, 255).

<sup>5</sup> Monnier, *Arch. Sci. phys. nat.*, 1916, iv., 42, 210.

<sup>6</sup> de Koninck, *Pharm. Zeit.*, 1889, 78, 594; Hillebrand, *Bull. U.S. Geol. Survey*, 1900, 176, 80; Richardson, Mann, and Hanson, *J. Soc. Chem. Ind.*, 1903, 22, 614.

<sup>7</sup> Horn, *Amer. Chem. J.*, 1906, 35, 253; Dittrich, *Zeitsch. anorg. Chem.*, 1913, 80, 171.

<sup>8</sup> Cazeneuve, *Zeitsch. angew. Chem.*, 1900, 13, 958; *Bull. Soc. chim.*, 1901, [3], 25, 758; Moulin, *ibid.*, 1904, [3], 31, 295; *Chem. News*, 1904, 89, 268.

The colour reaction with  $\alpha$ -naphthylamine (see p. 105) may also be used quantitatively.

*Electrolytic Methods.*—As yet, little success has attended the application of electrolysis to chromium compounds (*cf.* p. 10), but in the analysis of chrome yellow, and of other pigments with a basis of lead chromate, the lead may be separated by the electrolysis of a solution in nitric acid, and the chromium remaining in the solution then estimated in the usual way.<sup>1</sup>

<sup>1</sup> Jaroslav, Milbauer, and Ivan Šetlík, *J. prakt. Chem.*, 1919, [2], 99, 85.

## CHAPTER IV.

### MOLYBDENUM.

Symbol, Mo. Atomic weight, 96.0.

**Occurrence.**—Of the minerals containing molybdenum, the most important are *molybdenite* and *wulfenite*. The former consists essentially of the sulphide  $\text{MoS}_2$ , and occurs in a crystalline (hexagonal) form in granite, gneiss, granular limestone, etc. Its density is 4.75. It was formerly confused with graphite, which it resembles in appearance, but the difference was pointed out by Scheele in 1778–79. An artificial “molybdenite” has been prepared.<sup>1</sup> Molybdenite is widely, though sparingly, distributed, and is found in the following countries in the British Empire: Australia (chiefly Queensland and New South Wales), New Zealand, Canada and Newfoundland, Virgin Isles, Ceylon, Federated Malay States (not worked), India (not worked), Union of S. Africa (Natal, Transvaal), United Kingdom (Cornish mines, Inverness, Leicester, Cumberland). It occurs also in Austria, France, Germany, Russia, Norway, Sweden, the United States, Japan, and Mexico.<sup>2</sup> Wulfenite, *melinose*, or yellow lead spar, is lead molybdate,  $\text{PbMoO}_4$ . It occurs in veins with other lead ores in Austria, Hungary, Scotland, Siberia, and the United States. The brilliant red crystals of adamantinite lustre, which have a density of 6.85, belong to the tetragonal system. Wulfenite is a member of the scheelite (see p. 182) group of minerals.

*Molybdite* or *molybdenum ochre* forms orthorhombic<sup>3</sup> crystals, and occurs with molybdenite, from which it is probably derived. It consists essentially of the trioxide  $\text{MoO}_3$ , but analysis has shown<sup>4</sup> that its composition is probably expressed by the formula  $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ ; it being, in fact, a hydrated ferric molybdate. The sample examined was of a yellow colour, possessed a fibrous structure and a silky lustre, and was pleochroic.

Other minerals containing molybdenum are very rare. *Powellite*, calcium molybdate,  $\text{CaMoO}_4$ , containing calcium tungstate,  $\text{CaWO}_4$ , is a brittle mineral from Idaho. The crystals belong to the tetragonal system; density 4.53. *Belonesite*, which occurs in Vesuvian lava,<sup>5</sup> is essentially magnesium molybdate,  $\text{MgMoO}_4$ ; *pateraite*, a molybdate of iron and cobalt; *eosite*, a vanado-molybdate of lead; while one of the

<sup>1</sup> de Schulten, *Geol. För. Förhandl.*, 1889, 11, 401.

<sup>2</sup> See Imperial Institute Technical Information Bureau's pamphlet on *The Sources and Uses of Molybdenum Ores*, London, 1915.

<sup>3</sup> Nordenskjöld gives  $a : b : c = 0.3874 : 1 : 0.4747$ .

<sup>4</sup> Guild, *Amer. J. Sci.*, 1907, [4], 23, 455; Schaller, *ibid.*, 1907, [4], 23, 297; *Zeitsch. Kryst. Min.*, 1907, 44, 9.

<sup>5</sup> Scacchi, *Zeitsch. Kryst. Min.*, 1883, 14, 523.

constituents of *achrematite* is lead molybdate. *Ilsemanite*, a blue oxide, and molybdates of iron and uranium, are also found in nature.<sup>1</sup> The element has been detected in soot and dust produced by the combustion of coal obtained from the Liège district.<sup>2</sup>

**History.**—In view of their similarity in appearance, it is not surprising that in early times such substances as molybdenite and plumbago should have been confused with galena. That such was the case is reflected in the names “black lead” and “molybdœna” (*μόλυβδος*, lead), and the difference between the two substances was first pointed out in 1778–79 by Scheele in his treatises on “Molybdœna” and “Plumbago.” During his investigations on the composition of the former, Scheele heated it with nitric acid and obtained an acid-forming oxide; the subject was studied by Bergman (1781) and Hjelm, who isolated the metal in 1782.<sup>3</sup> The pure metal, free from carbon, was first obtained by Berzelius<sup>4</sup> by reduction of the oxide with hydrogen. The true composition of wulfenite was first demonstrated by Klaproth in 1797.

The most important researches on molybdenum compounds previous to 1880 were those of Svanberg and Struve (1848), and Ullik (1867), on the molybdates, and of Blomstrand (1857) on the halogen compounds. During the last half century much attention has been paid to the chemistry of molybdenum, and although our knowledge of the lower oxidation products of the element is still restricted, the nature of the many series of complex compounds has to a great extent been elucidated.

**Preparation.**—Although the purest molybdenum is obtained from wulfenite, the chief commercial source is molybdenite, which is converted into the trioxide by roasting in air either with or without the addition of sand, and, on dissolving the residue in ammonia, a solution of ammonium molybdate is obtained. This salt, freed from copper by treatment in ammoniacal solution with ammonium sulphide, and from aluminium by the addition of potassium carbonate, on ignition yields molybdenum dioxide; alternatively, heating with excess of sulphur yields pure molybdenum disulphide,  $\text{MoS}_2$ , which on roasting, or by treatment with nitric acid, is converted into the trioxide  $\text{MoO}_3$ .<sup>5</sup>

Though usually prepared in the metallic condition by Goldschmidt's process, molybdenum may also be obtained by the reduction of the oxide, sulphide, or halide, by treatment under suitable conditions with carbon, hydrogen, or other reducing agent; by an electrolytic method; or by heating the nitride *in vacuo*.

<sup>1</sup> See also Wöhler, *Mineral analysen* (Göttingen, 1855), pp. 167, 170; Heine, *J. prakt. Chem.*, 1834, [1], 9, 204; Mazade, *Compt. rend.*, 1851, 32, 685; Ogawa, *J. Coll. Sci. Tokyo*, 1908, 25, xvi., 1; Nasini and Baschieri, *Atti R. Accad. Lincei*, 1912, [5], 21, i., 692; Jorissen, *Bull. Soc. chim. Belg.*, 1913, 27, 21; Ferguson, *Amer. J. Sci.*, 1914, [4], 37, 399.

<sup>2</sup> Jorissen, *Bull. Soc. chim. Belg.*, 1913, 27, 21.

<sup>3</sup> Scheele, *Königl. Vet. Akad. Handl.*, 1778, p. 247; Hjelm, *ibid.*, 1790, 50, 81; *Crell's Annalen*, 1790, i., 39; 1791, i., 179, 248, 266, 353, 429; ii., 59; 1792, i., 260; ii., 358; 1794, i., 238.

<sup>4</sup> Berzelius, *Schweigger's J.*, 1817, 22, 51; *Ann. Chim. Phys.*, 1821, [2], 17, 5; *Pogg. Annalen*, 1825, 4, 153; 1826, 6, 331, 369; 7, 261.

<sup>5</sup> For further details of the processes used, a treatise on metallurgy must be consulted. See also Brunner, *Dingl. poly. J.*, 1858, 150, 672; Svanberg and Struve, *J. prakt. Chem.*, 1848, 44, 264; Delffs, *Annalen*, 1858, 106, 376; Wittstein, *Repertorium für Pharmacie*, 1852, [2], 73, 155. Cf. Wicke, *Annalen*, 1843, 45, 373; Wöhler, *ibid.*, 1843, 45, 374; Christl, *Dingl. poly. J.*, 1852, 124, 398; Elbers, *Annalen*, 1852, 83, 219.

1. *By Reduction of the Oxide with Aluminium Powder (Goldschmidt's Process).*—From the trioxide,  $\text{MoO}_3$ , a good yield of molybdenum free from air-bubbles can be obtained by Goldschmidt's method, it being preferable to moderate the reaction by the addition of a flux of 50 parts of calcium fluoride for every 100 parts of molybdenum trioxide, and 38 parts of aluminium, and to allow the metal to agglomerate by keeping the mass in a liquid condition for some time after the reaction.<sup>1</sup> Fused molybdenum may also be conveniently obtained by reduction with aluminium powder of the dioxide  $\text{MoO}_2$ , the latter being prepared by the reduction in hydrogen of the trioxide, or by ignition of ammonium molybdate,  $(\text{NH}_4)_2\text{MoO}_4$ .<sup>2</sup>

2. *By Reduction of the Oxide or Sulphide with Carbon.*—Molybdenum containing 4 to 5 per cent. of carbon is prepared by reduction of oxides of molybdenum by means of carbon in brasqued crucibles.<sup>3</sup> By reduction of 10 parts of the dioxide (obtained by ignition of ammonium molybdate) with 1 part of sugar charcoal in the electric furnace, using 800 amperes at 60 volts for six minutes, Moissan<sup>4</sup> obtained the metal, from which carbon was removed by heating with molybdenum dioxide, in a fairly pure condition, while by a similar process molybdenite,  $\text{MoS}_2$ , yields a metallic product free from sulphur but containing a little iron.<sup>5</sup> A mixture of molybdenite, lime, and fluorspar, heated in the electric furnace with a current of 70 to 100 amperes at 30 to 40 volts, produces a good yield of the homogeneous metal, though a purer product, containing 98.95 per cent. molybdenum, results if the mineral is first treated with concentrated hydrochloric acid.<sup>6</sup>

3. *Reduction of the Oxides, Halides, or Sulphides with Hydrogen.*—Molybdenum trioxide, purified by sublimation in a platinum tube, is heated in pure hydrogen first at as low a temperature as possible in order to convert it to the dioxide  $\text{MoO}_2$ , and finally in hydrogen in a quartz or platinum tube at a high temperature in order to complete the reduction.<sup>7</sup> Certain modifications in the technique of the process have been described.<sup>8</sup>

A brilliant steel-coloured form of the metal is obtained by reduction of chlorides of molybdenum at a red heat in a glass tube by hydrogen.<sup>9</sup> It is found<sup>10</sup> that molybdenum tetra- and penta-chlorides, on heating below  $1330^\circ \text{C}$ ., yield metallic molybdenum.

<sup>1</sup> Rosenheim and Braun, *Zeitsch. anorg. Chem.*, 1905, 46, 311.

<sup>2</sup> Biltz and Gärtner, *Ber.*, 1906, 39, 3370. See also Stavenhagen, *ibid.*, 1899, 32, 3065.

<sup>3</sup> Hjeltn, *K. Svenska Vet. Akad. Handl.*, 1788, p. 280; Bucholz, *ibid.*, 1825, p. 145; Debray, *Compt. rend.*, 1858, 46, 1098; Loughlin, *Amer. J. Sci.*, 1843, [2], 45, 31. The last named used potassium cyanide.

<sup>4</sup> Moissan, *Compt. rend.*, 1893, 116, 1225; 1895, 120, 1320.

<sup>5</sup> Guichard, *ibid.*, 1896, 122, 1270.

<sup>6</sup> Muthmann, Weiss, and Mai, *Annalen*, 1907, 355, 100. If the current used is 600 to 800 amperes at 110 volts, no metal is obtained, but instead, bluish-black crystals of molybdenum sesquisulphide,  $\text{Mo}_2\text{S}_3$ , are produced.

<sup>7</sup> Wöhler, *Annalen*, 1855, 94, 255; Rammelsberg, *Pogg. Annalen*, 1866, 127, 284; Debray, *Compt. rend.*, 1868, 66, 732.

<sup>8</sup> Meyer and Haas, *Ber.*, 1873, 6, 991; Liechti and Kempe, *Annalen*, 1873, 169, 314; Guichard, *Ann. Chim. Phys.*, 1901, [7], 23, 507; van der Berghe, *Bull. Acad. roy. Belg.*, 1895, [3], 30, 327; Svanberg and Struve, *J. prakt. Chem.*, 1848, [1], 44, 302; Rammelsberg, *ibid.*, 1866, [1], 97, 174; Sabatier and Senderens, *Bull. Soc. chim.*, 1892, [3], 7, 503; Moissan, *Ann. Chim. Phys.*, 1880, [5], 21, 1490; Müller, *J. Amer. Chem. Soc.*, 1915, 37, 2046.

<sup>9</sup> Wöhler and Uslar, *Annalen*, 1855, 94, 256.

<sup>10</sup> Pring and Fielding, *Trans. Chem. Soc.*, 1909, 95, 1504.



Reduction of the sulphides  $\text{MoS}_2$  or  $\text{MoS}_3$  in a Rose crucible by means of hydrogen also yields the metal.<sup>1</sup>

4. *Other Methods*.—Electrolysis of a solution of molybdic acid in hydrochloric acid, using a mercury cathode, yields an amalgam, from which an active form of molybdenum is obtained on distillation.<sup>2</sup>

On heating molybdenum oxide or its mixture with the metal to  $500^\circ$  to  $600^\circ$  C. with equal parts of nitrogen and hydrogen under a pressure of 60 atmospheres, a nitride is obtained which, when heated in a vacuum, leaves a residue of pure metallic molybdenum.<sup>3</sup>

**Physical Properties.**—In the massive metallic condition, pure molybdenum is a white malleable substance, not sufficiently hard to scratch glass, and of density, at  $26^\circ$  C.,  $10.281$ .<sup>4</sup> At  $20^\circ$  C. its compressibility is  $5.47 \times 10^{-6}$  per megabar.<sup>6</sup> The following values have been obtained<sup>7</sup> for the specific heat of molybdenum :

Temperature, ° C.	Specific Heat.
20 to 550	0.07219 <sup>8</sup>
20 „ 100	0.06468 <sup>8</sup>
-188 „ +20	0.0555 <sup>9</sup>
-253 „ -196	0.0141 <sup>10</sup>

The mean coefficient of expansion of molybdenum for the temperature range  $25^\circ$  C. to  $100^\circ$  C. is  $11.4.9 \times 10^{-6}$ , while for the range  $25^\circ$  C. to  $500^\circ$  C. the mean coefficient is  $5.5 \times 10^{-6}$ .

Molybdenum is paramagnetic. Numerous determinations of the magnetic susceptibility have been made, but the results obtained are widely divergent.<sup>12</sup> When obtained in the form of a powder it is grey in colour and lustreless, though the strongly compressed powder exhibits metallic lustre. The metal melts at  $2450 \pm 30^\circ$  C.,<sup>13</sup> and may, though with difficulty, be distilled in the electric furnace.<sup>14</sup>

The emission of electrons from molybdenum has been observed.<sup>15</sup>

<sup>1</sup> von der Pfordten, *Ber.*, 1884, 17, 732.

<sup>2</sup> Férée, *Compt. rend.*, 1896, 122, 733.

<sup>3</sup> Badische Anilin und Soda Fabrik, *German Patent*, 246554; *J. Chem. Soc.*, *Abstr.*, 1912, ii., 946.

<sup>4</sup> Müller, *J. Amer. Chem. Soc.*, 1915, 37, 2046. Wolf (*Dissertation, Tech. Hochschule Aachen*, 1918; *Chem. Zentr.*, 1918, i., 608) gives the density of pure molybdenum as 8.95. Moissan, *Compt. rend.*, 1895, 120, 1322, gives 9.01. See also Longhlin, *Amer. J. Sci.*, 1843, [2], 45, 31; Bucholz, *K. Svenska Vet.-Akad. Handl.*, 1825, p. 145; Debray, *Compt. rend.*, 1858, 46, 1098; Hjelm, *K. Svenska Vet.-Akad. Handl.*, 1788, p. 280—all of whom give figures less than that of Moissan, who used the pure electrically fused metal.

<sup>5</sup> Richards and Bartlett, *J. Amer. Chem. Soc.*, 1915, 37, 470.

<sup>6</sup> One megabar is 1000/g, where  $g$  is acceleration due to gravity. Whence, if  $g = 980.6$ , 1 megabar = 0.987 atmosphere at sea level  $45^\circ$  latitude.

<sup>7</sup> Earlier data are those of Regnault, *Ann. Chim. Phys.*, 1840, [2], 73, 49; Defacqz and Guichard, *ibid.*, 1901, [7], 24, 139.

<sup>8</sup> Stücker, *Wien Ber.*, 1905, 114, (2), 657.

<sup>9</sup> Richards and Jackson, *Zeitsch. physikal. Chem.*, 1910, 70, 414.

<sup>10</sup> Dewar, *Proc. Roy. Soc.*, 1913, A, 89, 158.

<sup>11</sup> Hidnert and Gero, *U.S. Bureau of Standards, Sci. Paper*, No. 488, 1924.

<sup>12</sup> Meyer, *Wied. Annalen*, 1899, 68, 324; Honda, *Ann. Physik*, 1910, [4], 32, 1027; Owen, *ibid.*, 1912, [4], 37, 657. Honda gives the value  $+0.04$  at  $18^\circ$  C.

<sup>13</sup> Pirani and Meyer, *Ber. Deut. physikal. Ges.*, 1912, 14, 426. Previous determinations were:  $2110^\circ$  C. (Ruff, *Ber.*, 1910, 43, 1564);  $>2550^\circ$  C. (Wartenberg, 1910). Wolf, *loc. cit.*, gives the freezing-point of pure liquid molybdenum  $2250^\circ$  C.

<sup>14</sup> Moissan, *Compt. rend.*, 1906, 142, 425.

<sup>15</sup> Dushman, Rowe, and Kidner, *Phys. Review*, 1923, 21, 207.

**Spectrum.**—The flame, arc, and spark spectra of molybdenum, which exhibit close similarity to those of chromium,<sup>1</sup> have been the subject of much careful investigation.<sup>2</sup> The most *persistent* lines are in the more refrangible part of the spectrum. The spark spectra of ammonium molybdate in both acid and alkaline solution have been photographed,<sup>3</sup> with identical results. The lines recorded were as follows : <sup>4</sup>

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
5570.7	10 $\sigma$	3176.4	4 $\chi$	2863.9	4 $\chi$
5533.3	10 $\sigma$	3175.2	4 $\chi$	2853.3	6 $\chi$
5506.7	10 $\sigma$	3173.0	4 $\chi$	2848.4	8 $\psi$
4760.4	6 $\phi$	3159.4	2 $\sigma$	2816.3	8 $\psi$
4731.6	4 $\phi$	3155.8	4 $\sigma$	2807.8	6 $\phi$
4707.4	4 $\phi$	3145.9	2 $\sigma$	2785.1	4 $\psi$
4381.8	4 $\chi$	3141.9	4 $\sigma$	2780.1	6 $\sigma$
4244.9	4 $\phi$	3141.6	4 $\sigma$	2775.5	6 $\omega$
3903.1	10 $\psi$	3139.0	4 $\sigma$	2746.4	5 $\phi$
3864.2	10 $\psi$	3132.9	4 $\phi$	2717.4	4 $\phi$
3798.4	10 $\psi$	3132.7	4 $\phi$	2684.2	4 $\psi$
3688.4	10 $\chi$	3111.0	4 $\phi$	2681.5	4 $\psi$
3614.4	4 $\sigma$	3092.2	4 $\phi$	2673.4	4 $\psi$
3524.7	6 $\chi$	3087.7	6 $\phi$	2660.6	4 $\psi$
3402.9	2 $\chi$	3077.7	6 $\phi$	2653.4	4 $\phi$
3254.8	4 $\chi$	2963.9	4 $\phi$	2646.6	4 $\chi$
3253.9	4 $\chi$	2923.5	4 $\chi$	2644.4	4 $\chi$
3244.6	1 $\sigma$	2912.0	4 $\phi$	2638.9	4 $\chi$
3240.8	4 $\chi$	2903.1	6 $\phi$	2602.9	5 $\phi$
3237.96	2 $\chi$	2894.5	4 $\chi$	2600.3	5 $\phi$
3223.1	2 $\sigma$	2888.3	4 $\chi$	2595.5	4 $\phi$
3209.0	2 $\sigma$	2879.1	6 $\phi$		
3200.4	4 $\chi$	2871.6	6 $\psi$		
3196.0	4 $\chi$	2866.8	5 $\sigma$		
3192.3	4 $\chi$				

Exner and Haschek (*loc. cit.*) record the most *intense* lines of the arc and spark spectra of molybdenum as follows : <sup>5</sup>

<sup>1</sup> Catalán, *Anal. Fis. Quim.*, 1923, 21, 213, 527; *Compt. rend.*, 1923, 176, 247, 1063.

<sup>2</sup> For the arc spectrum, region 23132 to 26031, see Exner and Haschek, *Die Spektren der Elemente bei normalem Druck*, Leipzig and Wien, 1911; 22420 to 24888, Pohlmann, *Zeitsch. wiss. Photochem.*, 1917, 17, 97; 24647 to 27134, Weigand, *ibid.*, 1912, 11, 261; 25500 to 29721, Kiess and Meggers, *Bureau of Standards Bull.*, 1920, 16, 51; *Sci. Paper*, p. 272. On the Zeeman effect, see Jack, *Proc. Roy. Soc. Edin.*, 1909, 29, 75; Catalán, *loc. cit.* The X-ray spectrum has been studied by Overn, *Phys. Review*, 1921, 17, 350; Duane and Patterson, *Proc. Nat. Acad. Sci.*, 1922, 8, 85; Tanaka and Tsutsumi, *Mem. Coll. Sci. Kyoto*, 1923, 7, 1. Earlier investigations by Hasselberg, *K. Svenska Vet.-Akad. Handl.*, 1903, 36, 2; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1895, 104; Lockyer, *Proc. Roy. Soc.*, 1878, 27; Thalen, *Nordica Acta Soc. Upsala*, 1868, 111.

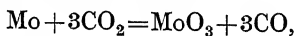
<sup>3</sup> Leonard, *Sci. Proc. Roy. Publ. Soc.*, 1908, 11, 270.

<sup>4</sup> For a general description of the methods employed, and an explanation of the abbreviations used, see p. 14.

<sup>5</sup> Refer to p. 13.

Arc Spectrum.		Spark Spectrum.	
Wave-length.	Intensity.	Wave-length.	Intensity.
3132.70	30 <i>u</i> *	2644.40	12
3170.46	20 <i>u</i> *	2775.47	15
3194.11	20 <i>u</i>	2816.22	20
3798.41	50 <i>u</i> *	3635.38	20
3864.30	50 <i>u</i>	3688.49	15
3903.11	30 <i>u</i> *	3798.41	20 <i>u</i> *
4411.86	20	3864.24	20
5360.80	20 +	3961.62	15
5506.62	50 + *	5360.80	15 +
5533.21	30 *	5506.70	30 *
5570.69	20 +	5533.28	20
5751.63	20 *	5570.70	15 *
5888.50	20 *	5888.52	15 *
5929.00	20	5928.03	20 +
[6030.80]	2	6030.89	20
6030.87	30		

**Chemical Properties.**—Molybdenum is not appreciably oxidised in air at ordinary temperatures, but at a dull red heat the trioxide,  $\text{MoO}_3$ , is slowly formed, the oxidation taking place more rapidly at  $600^\circ \text{C}$ . In oxygen alone vigorous combustion takes place at  $500^\circ$  to  $600^\circ \text{C}$ . Oxidation can be effected also by fusion with potassium chlorate, or less violently with potassium nitrate. The metal is attacked by fused, but not by aqueous, caustic alkali.<sup>1</sup> When heated in steam, it is converted first into the dioxide and then into the trioxide; <sup>2</sup> in a mixture of hydrogen and water-vapour, under suitable conditions, the dioxide is formed.<sup>3</sup> By fluorine it is attacked at ordinary temperatures, by chlorine at a dull red heat, by bromine at a red heat, but in the case of iodine there is no reaction. With hydrogen sulphide at  $1200^\circ \text{C}$ . the sulphide is formed. Molybdenum does not combine directly with hydrogen, nitrogen,<sup>4</sup> or phosphorus, but with boron, carbon, and silicon, compounds are formed. For this reason crystalline carbides are always formed when molybdenum is heated in carbon crucibles in the electric furnace.<sup>5</sup> Molybdenum may be oxidised to the trioxide by means of carbon dioxide,



but the reaction is reversible, and under suitable conditions the trioxide may be reduced to the metal by carbon monoxide; <sup>6</sup> the metal is volatile in carbonyl chloride.<sup>7</sup>

<sup>1</sup> See Ruder, *J. Amer. Chem. Soc.*, 1912, 34, 387.

<sup>2</sup> Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 356.

<sup>3</sup> Guichard, *ibid.*, 1901, [7], 23, 507; Chaudron, *Compt. rend.*, 1920, 170, 182.

<sup>4</sup> On the effect of heating a molybdenum filament in nitrogen at low pressures, see Langmuir, *J. Amer. Chem. Soc.*, 1919, 41, 167.

<sup>5</sup> Moissan, *Le four électrique*, 1st edn., 1897, p. 227; du Jassonneix, *Compt. rend.*, 1906, 143, 169; Tuttle, *Annalen*, 1857, 101, 285.

<sup>6</sup> Vandenberghe, *Zeitsch. anorg. Chem.*, 1896, 11, 397.

<sup>7</sup> Smith and Oberholzer, *ibid.*, 1894, 5, 63. For other reactions, see Smith, *ibid.*, 1892, 1, 360.

Molybdenum is, generally speaking, somewhat resistant to the action of acids, but is less so than tungsten.<sup>1</sup> It is untouched by hydrofluoric acid, hot or cold, and concentrated hydrochloric and sulphuric acids attack it only very slowly, the latter at elevated temperatures evolving sulphur dioxide, with the production of a green solution. Hot dilute hydrochloric acid slowly dissolves the metal, but sulphuric acid under similar conditions does not do so. Moderately dilute nitric acid attacks the metal rapidly; the concentrated acid induces a condition of passivity, the action being slow owing to the deposition of a film of molybdic anhydride,  $\text{MoO}_3$ , upon the surface of the metal. Aqua regia attacks the metal rapidly, particularly on heating.<sup>2</sup>

An especially active form of molybdenum has been obtained<sup>3</sup> by electrolysis of a solution of molybdenum trioxide in hydrochloric acid, using a mercury cathode, the mercury being removed from the amalgam formed by distillation.

**Atomic Weight.** For reasons similar to those applying in the case of chromium (p. 16), the atomic weight of molybdenum is three times the equivalent of the metal in the molybdic salts, or six times that in the molybdates. Molybdenum may be di-, tri-, or hexa-valent.

The results of investigations concerning the atomic weight of molybdenum are as follows :<sup>4</sup>

Date.	Investigators. <sup>5</sup>	Ratio Determined.	Atomic Weight.
1818	Berzelius . . .	$\text{PbMoO}_4 : \text{Pb}(\text{NO}_3)_2$	95
1837	Rose . . .	$\text{MoO}_2\text{Cl}_2 : \text{AgCl}$	99.4
		$\text{MoS}_2 : \text{AgCl}$	93.0
1848	Svanberg and Struve {	$\text{MoO}_3 : \text{CO}_2$	91.9
		$\text{MoS}_2 : \text{MoO}_3$	93.3
1850	Berlin . . .	$\text{NH}_4\text{Mo}_6\text{O}_{17} \cdot 3\text{H}_2\text{O} : 5\text{MoO}_3$	92.1
1858	Dumas . . .	$\text{MoO}_3 : \text{Mo}$	95.9
1868	Debray . . .	$\text{MoO}_3 : \text{Mo}$	95.4
1873	Lothar Meyer . . .	Analyses of chlorides	near 96
1873	Liechti and Kempe {		
1876	Rammelsberg . . .	$\text{MoO}_3 : \text{Mo}$	96.18
1893	Smith and Maas . . .	$\text{Na}_2\text{MoO}_4 : 2\text{NaCl}$	96.03
1895	Seubert and Pollard {	$2\text{AgCl} : \text{MoO}_3$	95.92
		$\text{MoO}_3 : \text{Mo}$	95.97
1898	Vandenberghc . . .	$\text{MoO}_3 : \text{Mo}$	96.06
		$\text{MoO}_3 : \text{Mo}$	96.02
1915	Müller . . .	$\text{MoO}_3 : \text{Mo}$	96.02
		$\text{MoO}_3 : \text{Mo}$	96.05

<sup>1</sup> Ruder, *J. Amer. Chem. Soc.*, 1912, 34, 387.

<sup>2</sup> Ruder, *loc. cit.*; Marino, *Gazzetta*, 1905, 35, [2], 193.

<sup>3</sup> Férée, *Compt. rend.*, 1896, 122, 733.

<sup>4</sup> The atomic weights have been recalculated from the following fundamental values : O, 16.000; H, 1.00762; N, 14.008; Cl, 35.457; C, 12.003; S, 32.065; Ag, 107.880; Pb, 207.20; Na, 22.996.

<sup>5</sup> Berzelius, *Schweigger's J.*, 1818, 22, 51; 23, 186; *Pogg. Annalen*, 1826, 8, 1; Rose, *ibid.*, 1837, 40, 400; Svanberg and Struve, *J. prakt. Chem.*, 1848, 44, 301; Berlin, *ibid.*, 1850, 49, 444; Dumas, *Annalen*, 1858, 105, 84; 1860, 113, 23; *Ann. Chim. Phys.*, 1859, [3], 55, 129, 142; Debray, *Compt. rend.*, 1868, 66, 734; Lothar Meyer, *Annalen*, 1873, 169, 365; Liechti and Kempe, *ibid.*, 1873, 169, 344; Rammelsberg, *Ber.*, 1876, 9,

The determinations made before 1858 may be ignored as of no modern significance. Those made since that date yield three ratios, from which the atomic weight of molybdenum may be calculated, namely :

- (1)  $\text{Na}_2\text{MoO}_4 : 2\text{NaCl} = 100 : 56.744 \pm 0.0017$ ;
- (2)  $2\text{AgCl} : \text{MoO}_3 = 100 : 50.204 \pm 0.0017$ ;
- (3)  $\text{MoO}_3 : \text{Mo} = 100 : 66.708 \pm 0.0010$ .

The values so obtained are (1) 96.06, (2) 95.92, (3) 96.04, the general mean being 96.006.

It is to be observed that the low results of Seubert and Pollard may be accounted for by loss of molybdic anhydride by volatilisation during ignition. Special precautions were taken by subsequent investigators to prevent this. Müller first oxidised the pure metal to the trioxide by heating in oxygen, using a quartz vessel, and then reduced the oxide by heating in a current of pure dry hydrogen. He made eight experiments, using three different samples of molybdenum, and his results, as shown in the table, are practically identical with those of Vandenberghé, and of Smith and Maas. From these considerations the atomic weight of molybdenum appears to approximate to the value  $96.04 \pm 0.01$ . The International Committee (1925) gives the value

$$\text{Mo} = 96.0.$$

**Alloys.**<sup>1</sup>—The most important alloy of molybdenum is ferro-molybdenum, which is used as an addition to steel. The effect of molybdenum on steel is similar to that of tungsten, but is more marked ; the tensile strength is increased and the elastic limit raised.<sup>2</sup> For high-speed tool-steels molybdenum is often used in conjunction with tungsten. It has been found<sup>3</sup> that the addition of molybdenum in small quantities (up to 15 per cent.) to steel increases the liability to corrosion, especially in acid and salt solutions. An important use of steels containing 3 to 4 per cent. of molybdenum and 1.0 to 1.5 per cent. of carbon is for the manufacture of permanent magnets.<sup>4</sup>

With copper, molybdenum forms a greyish-red hard alloy,<sup>5</sup> of density 7.934.

Silver and gold do not alloy with molybdenum ;<sup>6</sup> platinum can take at least 16 per cent. of the metal into solid solution near the melting-point, but on cooling the molybdenum separates out.<sup>7</sup>

1577 ; 1877, 10, 1776 ; *Berlin Monatsber.*, 1877, p. 574 ; Smith and Maas, *J. Amer. Chem. Soc.*, 1893, 15, 397 ; Seubert and Pollard, *Zeitsch. anorg. Chem.*, 1895, 8, 434 ; Vandenberghé, *Acad. roy. Belg., Mém. Couronnés*, 1898, 56 ; Müller, *J. Amer. Chem. Soc.*, 1915, 37, 2046.

<sup>1</sup> For a complete bibliography up to 1902 of researches on alloys, see Sack, *Zeitsch. anorg. Chem.*, 1903, 35, 249.

<sup>2</sup> See Law, *Alloys and their Industrial Applications*, 1909, p. 246 (Griffin & Co., Ltd., London).

<sup>3</sup> Friend and Marshall, *J. Iron Steel Inst.*, 1914, 89, 503 ; Aitchison, *Trans. Chem. Soc.*, 1915, 107, 1531.

<sup>4</sup> On the electrochemical behaviour of molybdenum-iron alloys, see Tammann and Sotter, *Zeitsch. anorg. Chem.*, 1923, 127, 257.

<sup>5</sup> Hamilton and Smith, *J. Amer. Chem. Soc.*, 1901, 23, 151. Cf. Dreibholz, *Zeitsch. physikal. Chem.*, 1924, 108, 1.

<sup>6</sup> Dreibholz, *loc. cit.*

<sup>7</sup> See also Barus, *Amer. J. Sci.*, 1888, [3], 36, 427.

With *mercury*, alloys corresponding to the formulæ  $\text{MoHg}_9$ ,  $\text{MoHg}_2$ , and  $\text{Mo}_3\text{Hg}_3$  have been described.<sup>1</sup>

With *aluminium*, a number of alloys are formed, the compositions of which agree with the formulæ  $\text{Al}_7\text{Mo}$ ,  $\text{Al}_4\text{Mo}$ ,  $\text{Al}_3\text{Mo}$ ,  $\text{Al}_2\text{Mo}$ ,  $\text{AlMo}$ , and  $\text{AlMo}_4$ ; the existence of the alloy  $\text{AlMo}_{20}$  is also suspected.<sup>2</sup>

Alloys with chromium and with bismuth have been obtained in the electric furnace.<sup>3</sup>

Alloys of molybdenum with other elements are dealt with in other volumes of this series.<sup>4</sup>

<sup>1</sup> Férée, *Compt. rend.*, 1896, **122**, 733. See p. 114.

<sup>2</sup> Guillet, *ibid.*, 1901, **132**, 1322; **133**, 291; *Génie civil*, 1902, **41**, 139, 156, 169, 188; Michel, *Dissertation*, Göttingen, 1860; Moissan, *Compt. rend.*, 1896, **122**, 1302; *Bull. Soc. chim.*, 1896, [3], **15**, 1282; *Ann. Chim. Phys.*, 1896, [7], **9**, 337; Wöhler and Michel, *Annalen*, 1860, **115**, 102.

<sup>3</sup> Sargent, *J. Amer. Chem. Soc.*, 1900, **22**, 783; Haynes, *J. Ind. Eng. Chem.*, 1913, **5**, 189; Siedschlag, *Zeitsch. anorg. Chem.*, 1924, **131**, 191.

<sup>4</sup> See also Mo—Mn, Sargent, *loc. cit.*; Arrivant, *Compt. rend.*, 1906, **143**, 285, 464; Mo—Ni, Sargent, *loc. cit.*; Baar, *Zeitsch. anorg. Chem.*, 1911, **70**, 352; Dreibholz, *loc. cit.*; Mo—Co, Sargent, *loc. cit.*; Raydt and Tammann, *Zeitsch. anorg. Chem.*, 1913, **83**, 246; Haynes, *loc. cit.*; Mo—Co—Cr, Camp and Marden, *J. Ind. Eng. Chem.*, 1920, **12**, 998; Mo—Fe, Benneville, *J. Amer. Chem. Soc.*, 1894, **16**, 735; Carnot and Goutal, *Compt. rend.*, 1897, **125**, 148, 213; 1899, **128**, 207; *Ann. des Mines*, 1900, [9], **18**, 263; *Contribution à l'étude des alliages* (Paris, 1901), p. 493; Curie, *ibid.*, p. 157; Le Chatelier, *ibid.*, p. 413; Mathews, *J. Iron Steel Inst.*, 1902, **61**, 182; Guillet, *Compt. rend.*, 1904, **139**, 519; Vigouroux, *ibid.*, 1906, **142**, 889, 928; Lautsch and Tammann, *Zeitsch. anorg. Chem.*, 1907, **55**, 386; Trautmann, *Zeitsch. angew. Chem.*, 1911, **24**, 635; Mo—W, Geiss and van Liempt, *Zeitsch. anorg. Chem.*, 1923, **128**, 355.

## CHAPTER V.

### COMPOUNDS OF MOLYBDENUM.

#### GENERAL PROPERTIES OF MOLYBDENUM COMPOUNDS.

IN its most stable and most important compounds, molybdenum occurs as a hexavalent element. The trioxide  $\text{MoO}_3$ , corresponding to chromium trioxide, is markedly acidic,<sup>1</sup> forming salts which readily combine with further molecules of the acid oxide to form series of polymolybdates. The strongly electronegative character of hexavalent molybdenum is also exhibited in the acid nature of the sulphide, and the formation of thiomolybdates of the types  $\text{R}_2\text{S} \cdot \text{MoS}_3$  and  $\text{R}_2\text{S} \cdot 2\text{MoS}_3$ , and again in the difficulties encountered in attempts to isolate halogen compounds of the type  $\text{MoCl}_6$ , owing to the ready formation of complex anions containing molybdenum and the halogen. The trioxide readily combines with other acidic oxides, such as phosphorus pentoxide, arsenic pentoxide, and silica, forming series of complex heteropolyacids which give rise to well-defined crystalline salts. These compounds, in colour, isomorphism, and general properties, show a close relationship to the corresponding derivatives of tungsten.

The compounds containing molybdenum in lower stages of valency are much less stable than the fully oxidised derivatives, and in many cases further investigation is necessary before their constitution can be expressed with certainty. Normal salts containing divalent molybdenum are not known, but certain halogen compounds of amphoteric character do exist, of empirical formula  $\text{MoX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), but of molecular formula  $\text{Mo}_3\text{X}_6$ . These are insoluble in water, but the chloride and bromide yield acids of the type  $\text{HMo}_3\text{X}_7$ , salts of which have been prepared. Substituted compounds, such as  $\text{Mo}_3\text{Cl}_4(\text{OH})_2$  and  $\text{Mo}_3\text{Cl}_4(\text{NO}_3)_2$ , are also known. None of these substances in solution yield simple halogen ions, and the stability of the complex is indicated by the fact that they are unaffected by such oxidising agents as potassium nitrate.

Trivalent molybdenum is found in a few simple compounds. The black hydroxide,  $\text{Mo}(\text{OH})_3$ , dissolves in acids with salt formation, yielding reddish-purple solutions which darken in colour. Upon evaporation crystalline salts are not obtained, but when the solution is taken to dryness a greyish-black residue remains, which can be redissolved in water to a dark grey solution. This may be accounted for by the readiness with which the salts undergo hydrolysis, with formation of the black hydroxide, possibly in the colloidal form. The similarity of molybdenum to chromium is seen in the series of complex

<sup>1</sup> For indications of basic properties in the trioxide, see p. 137.

thiocyanates of the type  $R_3[Mo(CNS)_6].aq.$ , which are analogous to, and isomorphous with, the chromithiocyanates  $R_3[Cr(CNS)_6].aq.$

Few derivatives of molybdenum dioxide,  $MoO_2$ , have been prepared, and it is doubtful whether simple salts containing tetravalent molybdenum can be formed in solution. By the electrolytic reduction of acid molybdate solutions, brownish-coloured liquids apparently containing the metal in this stage of oxidation have been obtained, but the evidence is insufficient to determine whether  $Mo^{IV}$  ions are actually present, or whether the liquids merely contain mixed  $Mo^V$  and  $Mo^{III}$  ions. Potential measurements indicate the presence of mixed ions. The only simple substances containing tetravalent molybdenum, in addition to the oxide, are the sulphide,  $MoS_2$ , the tetrachloride,  $MoCl_4$ , and the tetrabromide,  $MoBr_4$ . There are, however, two series of complex molybdocyanides, of the types  $R_4[Mo(OH)_4(CN)_4].aq.$  and  $R_4[Mo(CN)_8].aq.$  respectively, which contain tetravalent molybdenum and yield well-crystallised salts. Their existence is probably due to the resistance of the stable complex to hydrolytic decomposition.

Pentavalent molybdenum occurs in the hydroxide  $Mo(OH)_5$ , which is obtained as a reddish-brown precipitate by addition of alkali to the red solution resulting from careful reduction of aqueous molybdic acid (see p. 131). The pentahydroxide is basic, but the only normal salt as yet obtained is the pentachloride, which is prepared in the dry way (see p. 125). Salts containing the *molybdenyl* radical  $MoO^{+++}$  are obtainable in the wet way; for example, a series of halogen double salts, of the type  $MoOX_3 \cdot 2R'X.aq.$  ( $X = F, Cl, Br$ ), is known. Complex thio-cyanates, of the form  $Mo(OH)_2(SCN)_3$ , have been obtained in combination with organic bases (see p. 173), whilst molybdicyanides, of the type  $R_3Mo(CN)_8$ , analogous to the corresponding tungsten compounds (see p. 171), have been described.

Highly oxidised compounds of molybdenum, usually obtained through the agency of hydrogen peroxide, are known; such, for example, are the permolybdates, fluoxypermolybdates, and the perthiomolybdates. In these compounds, however, the valency of the molybdenum appears to be 6, which may be considered as the maximum valency of the element. The constitution of the sulphur compounds, which are of the types  $R'MoS_5$  and  $R'MoS_6$ , has not as yet been established, and although a tetrasulphide,  $MoS_4$ , exists, there is no evidence that the molybdenum is functioning with higher valency than 6.

**Uses.** A few molybdenum compounds are used in the production of pigments and for producing a yellow colour in pottery glazes. Glass may be coloured yellow or red by the addition of molybdenum disulphide.<sup>1</sup> The blue oxide, *molybdenum blue* or *molybdenum indigo*, is used as a dye in the textile industry, especially for silk; it is also useful as a pigment for indiarubber. Ammonium molybdate finds employment in the analytical estimation of phosphoric acid, while molybdic acid is an important reagent for certain classes of organic substances. Molybdenum compounds are used to a small extent in photography.

#### MOLYBDENUM AND HYDROGEN.

No compound of molybdenum with hydrogen is known to exist.

<sup>1</sup> Zaigmondi, *Dingl. poly. J.*, 1889, 273, 29.



## MOLYBDENUM AND FLUORINE.

**Molybdenum Hexafluoride,  $\text{MoF}_6$ ,** the only fluoride known with certainty to exist, is best prepared<sup>1</sup> by the action of fluorine on the finely divided metal at  $60^\circ$  to  $70^\circ$  C., the product being collected in a vessel cooled by a mixture of solid carbon dioxide and alcohol. It forms white crystals which melt at  $17^\circ$  C., the boiling-point of the liquid being  $35^\circ$  C. It is decomposed by water, yielding the blue oxide (see p. 131), but does not react with chlorine, sulphur dioxide, or dry air; it is absorbed by alkali or ammonium hydroxides, and forms double salts with alkali fluorides. It also reacts with ammonia, with production of a brown powder.

Interaction of molybdenum pentachloride and anhydrous hydrogen fluoride yields a fluoride of molybdenum,<sup>2</sup> while the existence of fluorides of the formulæ  $\text{MoF}_3$  and  $\text{MoF}_4$  has been affirmed.<sup>3</sup> Double salts of the formulæ  $\text{KMoF}_4 \cdot \text{H}_2\text{O}$ ,  $(\text{NH}_4)\text{MoF}_4 \cdot \text{H}_2\text{O}$ ,  $\text{K}_3\text{Mo}_2\text{F}_9 \cdot 2\text{H}_2\text{O}$ , and  $(\text{NH}_4)_3\text{Mo}_2\text{F}_9 \cdot 2\text{H}_2\text{O}$  have been described.<sup>4</sup>

Two **oxyfluorides**, respectively  $\text{MoOF}_4$  and  $\text{MoO}_2\text{F}_2$ , have been prepared<sup>1</sup> by the action of anhydrous hydrogen fluoride upon the corresponding oxychlorides in a platinum vessel surrounded by a freezing mixture. The former compound,  $\text{MoOF}_4$ , which distils at  $230^\circ$  C., is a white hygroscopic solid, of melting-point  $97^\circ$  C. and boiling-point  $180^\circ$  C.; in air it decomposes, simultaneously becoming blue in colour. The latter compound,  $\text{MoO}_2\text{F}_2$ , which sublimates at  $265^\circ$  to  $270^\circ$  C., forms white hygroscopic crystals of density 3.494; with a little water it turns blue in colour, but with much water the mixture is colourless. Heated in air, it decomposes, evolving hydrogen fluoride and leaving a residue of molybdic anhydride. An alternative method of preparation of the oxyfluoride  $\text{MoO}_2\text{F}_2$  consists<sup>5</sup> in heating together molybdic anhydride and lead fluoride, cryolite, or other metallic fluoride in a stream of carbon dioxide or oxygen. Compounds of this oxyfluoride with metallic fluorides ("fluoroxymolybdates") are known.<sup>6</sup>

With *sodium*, the compound  $\text{MoO}_2\text{F}_2 \cdot 2\text{NaF} \cdot \frac{1}{2}\text{H}_2\text{O}$  is formed as a crystalline salt by treating the normal molybdate with a slight excess of hydrofluoric acid.<sup>6</sup> The *potassium* salts which have been prepared are  $\text{MoO}_2\text{F}_2 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$  and  $\text{MoO}_2\text{F}_2 \cdot \text{KF} \cdot \text{H}_2\text{O}$ ,<sup>7</sup> while to other compounds the following formulæ have been assigned:<sup>8</sup>  $\text{MoOF}_3 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$  and  $3\text{MoOF}_3 \cdot 5\text{KF} \cdot \text{H}_2\text{O}$ . With *rubidium*, the compound  $\text{MoO}_2\text{F}_2 \cdot \text{RbF} \cdot 2\text{H}_2\text{O}$  has been described,<sup>9</sup> as also have<sup>10</sup> the following compounds of *ammonium*:  $\text{MoO}_2\text{F}_2 \cdot 2\text{NH}_4\text{F}$ ;  $\text{MoO}_2\text{F}_2 \cdot \text{NH}_4\text{F}$ ;  $\text{MoO}_2\text{F}_2 \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$ ;

<sup>1</sup> Ruff and Eisner, *Ber.*, 1907, 40, 2926.

<sup>2</sup> Ruff and Eisner, *ibid.*, 1905, 38, 742.

<sup>3</sup> Berzelius, *Pogg. Annalen*, 1827, 9, 369; Mauro and Panebianco, *Ber.*, 1882, 15, 2510.

<sup>4</sup> Rosenheim and Braun, *Zeitsch. anorg. Chem.*, 1905, 46, 311; Rosenheim and Li, *Ber.*, 1923, 56, B, 2228.

<sup>5</sup> Schultze, *J. prakt. Chem.*, 1880, [2], 21, 442.

<sup>6</sup> Delafontaine, *Arch. Sci. phys. nat.*, 1867, 30, 233.

<sup>7</sup> Berzelius, *Ann. Chim. Phys.*, 1825, [2], 29, 369; Delafontaine, *loc. cit.*

<sup>8</sup> Mauro and Panebianco, *Ber.*, 1882, 15, 2510; Mauro, *Gazzetta*, 1892, 19, 179; Nordenskjöld, *Ber.*, 1901, 34, 1572.

<sup>9</sup> Blomstrand, *J. prakt. Chem.*, 1861, 82, 433.

<sup>10</sup> Mauro, *loc. cit.*; Delafontaine, *loc. cit.*

$3\text{MoO}_2\text{F}_2 \cdot 5\text{NH}_4\text{F} \cdot \text{H}_2\text{O}$ ;  $\text{MoO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$ ;  $\text{MoO}_2\text{F}_2 \cdot 4\text{NH}_4\text{F} \cdot (\text{NH}_4)_2\text{MoO}_4$ ;  $\text{MoO}_3 \cdot 2\text{NH}_4\text{F}$ ;  $\text{MoOF}_3 \cdot 2\text{NH}_4\text{F}$ ;  $3\text{MoOF}_3 \cdot 5\text{NH}_4\text{F} \cdot \text{H}_2\text{O}$ .<sup>1</sup>

**Fluoroxypermolybdates.**—When potassium fluoroxymolybdate  $\text{MoO}_2\text{F}_2 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$  is dissolved in warm hydrogen-peroxide solution, oxidation occurs, and on cooling, fine yellow laminae, of composition  $2\text{MoO}_3\text{F}_2 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$ , separate. This salt reduces potassium permanganate in dilute sulphuric acid solution, with evolution of oxygen. Corresponding cesium and rubidium salts have also been obtained. A solution of ammonium paramolybdate in hydrofluoric acid, when treated with hydrogen peroxide in presence of excess ammonium fluoride, yields on evaporation the compound  $\text{MoO}_3\text{F}_2 \cdot 3\text{NH}_4\text{F}$ , which may also be obtained by the direct action of hydrogen peroxide on the fluoroxymolybdate  $\text{MoO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$ .<sup>3</sup> By the further action of hydrogen peroxide on the potassium salt, the compound  $\text{MoO}_4 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$  may be obtained.<sup>4</sup>

### MOLYBDENUM AND CHLORINE.

**Molybdenum Dichloride.** The normal chloride of divalent molybdenum,  $\text{MoCl}_2$ , which in solution would yield the simple ions  $\text{Mo}^{++}$  and  $\text{Cl}^-$ , is not known. The so-called "molybdenum dichloride," which does contain the divalent metal, has been shown to be an amphoteric compound of more complex composition. It may be prepared by heating to redness the trichloride in a stream of dry carbon dioxide,<sup>5</sup> when the volatile tetrachloride distils, leaving a residue of the dichloride. Careful regulation of the temperature, and exclusion of air and moisture, are important,<sup>6</sup> or the product will contain higher chlorides and oxychlorides. The dichloride is also formed by heating molybdenum with mercurous chloride, or by passing chlorine largely diluted with carbon dioxide over the moderately heated metal; in both cases satisfactory yields are difficult to obtain. The most productive method appears to be the heating of molybdenum powder in a stream of carbonyl chloride at  $610^\circ$  to  $620^\circ \text{C}$ .<sup>7</sup> The dichloride remains as a heavy yellow powder, which may be extracted with ether containing 5 per cent. of absolute alcohol. After evaporation of the solution *in vacuo*, a light yellow stable powder, of composition  $\text{Mo}_3\text{Cl}_6 \cdot \text{C}_2\text{H}_5\text{OH}$ , remains, the alcohol in which cannot be removed by heating in an inert atmosphere without further decomposition taking place. The addition of alcoholic silver nitrate to a solution of the compound in alcohol precipitates silver chloride, and the mother-liquor on standing deposits the compound  $\text{Mo}_3\text{Cl}_4(\text{NO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$ ; immediate treatment of the mother-liquor with ether, however, causes separation of the alcohol-free compound  $\text{Mo}_3\text{Cl}_4(\text{NO}_3)_2$ . The formula for the chloride may therefore be written  $(\text{Mo}_3\text{Cl}_4)\text{Cl}_2$ .

If the original dichloride powder is extracted with concentrated hydrochloric acid, long yellow needles, of composition  $\text{Mo}_3\text{Cl}_6 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ ,

<sup>1</sup> For crystallographic data regarding a number of these compounds, see Groth, *Chemische Kristallographie*, 1906, vol. i.

<sup>2</sup> Piccini, *Zeitsch. anorg. Chem.*, 1892, **1**, 51; *Atti R. Accad. Lincei*, 1892, **7**, i., 267.

<sup>3</sup> Piccini, *loc. cit.*

<sup>4</sup> Kazanetsky, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 383.

<sup>5</sup> Blomstrand, *J. prakt. Chem.*, 1859, [1], **77**, 96; 1861, **82**, 423.

<sup>6</sup> Liechti and Kempe, *Annalen*, 1873, **169**, 344; Muthmann and Nagel, *Ber.*, 1898, **31**, 2009.

<sup>7</sup> Lindner and Co-workers, *Ber.*, 1922, **55**, B, 1458; *Zeitsch. anorg. Chem.*, 1923, **130**, 209.

may be separated almost quantitatively from the solution.<sup>1</sup> These in air lose hydrogen chloride, becoming green; when heated in a stream of hydrogen chloride the compound  $\text{Mo}_3\text{Cl}_6 \cdot \text{H}_2\text{O}$  results. The yellow crystalline substance acts as a chloracid containing the anion  $\text{Mo}_3\text{Cl}_7^-$ , its solution in the minimum quantity of hydrochloric acid yielding, with concentrated solutions of metallic chlorides, salts of composition  $\text{R}[\text{Mo}_3\text{Cl}_7] \cdot x\text{H}_2\text{O}$ .<sup>2</sup> The addition of dilute acid to a solution of the chloracid in dilute alkali precipitates a crystalline hydroxide of composition  $[\text{Mo}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}](\text{OH})_2 \cdot 6\text{H}_2\text{O}$ .<sup>3</sup> This formula is based on the behaviour of the compound on dehydration; at  $100^\circ \text{C}$ . 6 molecules of water are lost, a seventh is expelled below  $300^\circ \text{C}$ ., and the final product, which resists further dehydration, has the composition  $[\text{Mo}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}]\text{O}$ . With hydrobromic acid the hydroxide yields acids for which the following formulæ have been given:<sup>4</sup>  $\text{H}[\text{Mo}_3\text{Cl}_4\text{Br}_3 \cdot \text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$  and  $\text{H}_2[\text{Mo}_3\text{Cl}_4\text{Br}_4 \cdot 4\text{H}_2\text{O}]2\text{H}_2\text{O}$ ; salts of these acids have also been described.

Molybdenum "dichloride," that is, the chloracid  $\text{HMo}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$ , dissolves in aqueous alkali hydroxides forming yellow solutions which, on boiling, deposit the black dihydroxide  $\text{Mo}(\text{OH})_2$ .<sup>5</sup> The alcoholic solution conducts electricity, the molecular conductivity increasing on dilution; hydrogen, the oxychloride  $\text{Mo}_3\text{Cl}_4(\text{OH})_2$ , and sometimes molybdenum are liberated at the cathode, whilst acetaldehyde and ethyl chloride are formed at the anode.

**Molybdenum Trichloride,  $\text{MoCl}_3$ ,** is obtained by reduction of the pentachloride<sup>6</sup> by hydrogen at  $250^\circ \text{C}$ .; by passing the vapour of the pentachloride over the heated metal; or by passing a mixture of the pentachloride vapour and carbon dioxide through a heated tube. It is a reddish-brown amorphous substance, stable in air at ordinary temperatures, but on heating in air decomposes, leaving an impure residue of the dichloride.

The trichloride is insoluble in water and alcohol; by boiling water it is decomposed with hydrolysis. A solution may, however, be obtained<sup>7</sup> by electrolysis either of a solution of molybdic anhydride in hydrochloric acid, or of a solution of ammonium molybdate in dilute sulphuric acid, a mercury cathode being employed. The substance is dissolved by sulphuric and by nitric acids, but not by hydrochloric acid.<sup>8</sup> With gaseous ammonia, at  $340^\circ \text{C}$ . the compound  $\text{Mo}_2(\text{NH}_2)_3\text{Cl}_3$  is obtained, while at  $760^\circ \text{C}$ . the nitride  $\text{Mo}_3\text{N}_2$  is produced. A solution of ammonia gives a black, easily oxidisable compound  $\text{MoNH}_4\text{O}_4$ , while with liquid ammonia the products are<sup>9</sup>  $\text{Mo}_2(\text{NH}_2)_3\text{Cl}_3 \cdot 10\text{NH}_3$  and  $\text{Mo}_2(\text{NH}_2)_3\text{Cl}_3$ .

A hydrate of molybdenum trichloride has been stated to exist. By the action of potassium amalgam on a solution of molybdic acid in excess of hydrochloric acid, garnet-red, soluble prisms of the double

<sup>1</sup> Rosenheim and Kohn, *Zeitsch. anorg. Chem.*, 1910, 66, 1.

<sup>2</sup> Lindner and Co-workers, *loc. cit.*; Koppel, *Zeitsch. anorg. Chem.*, 1912, 77, 289; Rosenheim and Kohn, *loc. cit.*; Blomstrand, *loc. cit.*

<sup>3</sup> Lindner and Co-workers, *loc. cit.* Cf. Blomstrand, *loc. cit.*

<sup>4</sup> Lindner and Co-workers, *loc. cit.*

<sup>5</sup> Wolf, *Dissertation Tech. Hochschule Aachen*, 1918; *Chem. Zentr.*, 1918, i., 608.

<sup>6</sup> Blomstrand, *loc. cit.*; Wolf, *loc. cit.*

<sup>7</sup> Chilesotti, *Atti R. Accad. Lincei*, 1903, [5], 12, ii., 22, 67.

<sup>8</sup> Liechti and Kempe, *loc. cit.*

<sup>9</sup> Rosenheim and Braun, *Zeitsch. anorg. Chem.*, 1905, 46, 311.

chloride  $3KCl \cdot MoCl_3 \cdot 2H_2O$  are obtained.<sup>1</sup> Similar double salts, of composition  $K_3MoCl_6$  and  $2(NH_4)_3MoCl_6 \cdot 5H_2O$ , have been prepared<sup>2</sup> by electrolysing strongly acid solutions of molybdic acid, using a mercury cathode, adding the alkali chloride to the resulting purple-red solution, and evaporating. The compounds  $Rb_2MoCl_5 \cdot H_2O$ ,  $(NH_4)_2MoCl_5 \cdot H_2O$ , and  $Cs_2MoCl_5 \cdot H_2O$  have been prepared,<sup>3</sup> and the last named has been shown to exist in three different crystalline modifications.

**Molybdenum Tetrachloride,  $MoCl_4$ ,** may be prepared by the action of chlorine at a high temperature upon molybdenum, or upon the oxide or sulphide mixed with carbon;<sup>4</sup> by heating the trichloride to redness in a stream of dry carbon dioxide, both the tetrachloride and the dichloride of molybdenum are obtained, although the former does not distil without decomposition.

Molybdenum tetrachloride forms a semi-crystalline deliquescent powder, unstable in air, in which, if heated, it yields the oxychloride  $MoO_2Cl_2$  and dichlormolybdic acid  $MoO_3 \cdot 2HCl$ ; it is also stated to be converted spontaneously into the pentachloride and trichloride. If sufficiently heated—though below  $1330^\circ C.$ —it is reduced to the metal.<sup>5</sup> In water, alcohol, ether, and in dilute sulphuric acid it gives unstable solutions.

The double salt  $3MoCl_4 \cdot 2NH_4Cl \cdot 6H_2O$  has been described.<sup>6</sup>

**Molybdenum Pentachloride,  $MoCl_5$ ,** is best prepared by gently heating molybdenum in chlorine, when the former glows with production of a reddish vapour which somewhat readily dissociates. On cooling, the vapour yields black deliquescent crystals which melt at  $194^\circ C.$  and the resulting liquid boils at  $268^\circ C.$ <sup>7</sup> The compound is also produced by the interaction of molybdenum trioxide with phosphorus pentachloride.<sup>8</sup>

The pentachloride is a little unstable in air; when heated to about  $1330^\circ C.$  or less it leaves a residue of molybdenum;<sup>5</sup> when heated in hydrogen at  $250^\circ C.$  it is reduced to amorphous molybdenum trichloride. Its aqueous solution is unstable in air, especially on warming, when hydrogen chloride is more rapidly evolved and the blue oxide (p. 131) remains. Decomposition of its solution in hydrochloric acid also readily takes place.<sup>9</sup> In alcohol and ether it dissolves to a green solution; in sulphuric acid its solution is bluish green and in nitric acid colourless; alkalis dissolve it with production of the hydrated dioxide and a molybdate.<sup>10</sup>

**Oxychlorides.** Several have been described. The compounds  $Mo_2O_3Cl_2$  and  $Mo_3O_3Cl_7$  have been stated<sup>11</sup> to be formed by the reduction of the oxychloride  $MoOCl_4$  (see below).

The compound  $Mo_2O_3Cl_5$  was stated by Blomstrand<sup>12</sup> to be formed

<sup>1</sup> Henderson, *Proc. Chem. Soc.*, 1903, **19**, 245.

<sup>2</sup> Rosenheim and Li, *Ber.*, 1923, **56**, B, 2228.

<sup>3</sup> Chilesotti, *loc. cit.*

<sup>4</sup> Blomstrand, *J. prakt. Chem.*, 1857, **71**, 457; Debray, *Compt. rend.*, 1858, **46**, 1098. Debray attributed to this compound the formula  $MoCl_5$ . Cf. Liechti and Kempe, *Annalen*, 1873, **169**, 351.

<sup>5</sup> Pring and Fielding, *Trans. Chem. Soc.*, 1909, **95**, 1504.

<sup>6</sup> Blomstrand, *loc. cit.*

<sup>7</sup> Debray, *Compt. rend.*, 1868, **66**, 732; Wolf, *Dissertation Tech. Hochschule Aachen*, 1918; *Chem. Zentr.*, 1918, i, 608; Lindner and Co-workers, *Ber.*, 55, B, 1458.

<sup>8</sup> Ehrenfeld, *J. Amer. Chem. Soc.*, 1895, **17**, 381.

<sup>9</sup> Guichard, *Ann. Chim. Phys.*, 1901, [7], **23**, 507; Nordenskjöld, *Ber.*, 1901, **34**, 1572.

<sup>10</sup> See also Lloyd, *J. Physical Chem.*, 1913, **17**, 592.

<sup>11</sup> Putzbach, *Annalen*, 1880, **201**, 123.

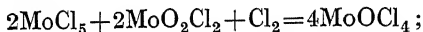
<sup>12</sup> Blomstrand, *J. prakt. Chem.*, 1857, **71**, 462.

as reddish-brown, fusible crystals by condensation of the brown vapours which are produced when chlorine is passed over heated molybdenum sesquioxide,  $\text{Mo}_2\text{O}_3$ .

The *oxychloride*  $\text{MoO}_2\text{Cl}_2$  is obtained when chlorides of molybdenum are heated in the air, and, among other compounds, when the dioxide, or a mixture of the trioxide with carbon, is heated in chlorine,<sup>1</sup> or when molybdenum trioxide and phosphorus trichloride are heated together;<sup>2</sup> it is *not* formed, however, when a mixture of common salt, sulphuric acid, and molybdenum trioxide is heated<sup>3</sup> (*cf.* p. 28). A pale yellow amorphous substance, soluble in water and alcohol, it is easily sublimed, and is reduced on heating in hydrogen or carbon monoxide to the dioxide.

The *compound*  $\text{Mo}_3\text{O}_5\text{Cl}_8$  is stated to be a stable red crystalline substance which is produced on heating the *compound*  $\text{Mo}_2\text{O}_3\text{Cl}_6$ ; the latter is a violet crystalline deliquescent body, soluble in water, produced by reduction in hydrogen of the oxychloride  $\text{MoOCl}_4$ .<sup>1</sup> It sublimes on heating; when heated in the air it is oxidised to the oxychloride  $\text{MoO}_2\text{Cl}_2$  and chlorine; its aqueous solution is unstable.

The *oxychloride*  $\text{MoOCl}_4$  is formed on heating in chlorine a mixture of molybdenum pentachloride and the compound  $\text{MoO}_2\text{Cl}_2$ :



or by using instead appropriate quantities of the metal and the dioxide. The substance is considered by Nordenskjöld<sup>4</sup> to be a mixture in varying proportions of the pentachloride with the oxychloride  $\text{MoO}_2\text{Cl}_2$ . The crystals obtained, on purification by sublimation, have a dark green colour and metallic lustre. They readily fuse and vaporise, and are affected by sunlight. The aqueous solution is unstable; on heating alone, the compound  $\text{Mo}_2\text{O}_3\text{Cl}_6$  is formed; while in hydrogen it gives the oxychlorides  $\text{Mo}_3\text{O}_3\text{Cl}_7$  and  $\text{MoO}_2\text{Cl}_2$ , molybdenum dichloride and molybdenum.<sup>1</sup>

The following compounds have also been prepared:<sup>5</sup>  $\text{MoOCl}_3$ ,  $2\text{NH}_4\text{Cl}$ ,  $\text{MoOCl}_3 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ ,  $\text{MoOCl}_3 \cdot 2\text{RbCl}$ ,  $\text{MoOCl}_3 \cdot 2\text{CsCl}$ , together with similar compounds with certain organic bases.

**Chlormolybdic Acids.**—The compound  $\text{MoOCl}_2(\text{OH})_2$ , molybdenum hydroxychloride or dichlormolybdic acid, is readily obtained by passing hydrogen chloride over any heated oxygenated compound of molybdenum. Fine white unstable needles are obtained, the aqueous solution of which deposits on evaporation amorphous molybdic anhydride. The substance is also soluble in ether, with which it forms a crystalline compound.<sup>6</sup> An alternative method of preparation of dichlormolybdic acid consists in cooling a solution of molybdic acid saturated with hydrochloric acid.<sup>7</sup>

<sup>1</sup> Blomstrand, *J. prakt. Chem.*, 1857, 71, 462; Püttbach, *Annalen*, 1880, 201, 123.

<sup>2</sup> Schiff, *Annalen*, 1857, 102, 116; Michaelis, *Jahresber.*, 1871, 24, 249; Schultze, *J. prakt. Chem.*, 1880, [2], 21, 441.

<sup>3</sup> Rose, *Pogg. Annalen*, 1848, 75, 319.

<sup>4</sup> Nordenskjöld, *Ber.*, 1901, 34, 1572; Klason, *ibid.*, 1901, 34, 148.

<sup>5</sup> Klason, *loc. cit.*; Nordenskjöld, *loc. cit.*; Henderson, *Proc. Chem. Soc.*, 1903, 19, 245.

<sup>6</sup> Debray, *Compt. rend.*, 1858, 46, 1101; Péchard, *ibid.*, 1892, 114, 173; Vandenberghé, *Bull. Acad. roy. Belg.*, 1895, [3], 29, 281; Smith and Maas, *Zeitsch. anorg. Chem.*, 1894, 5, 280.

<sup>7</sup> Weinland and Knoll, *Ber.*, 1904, 37, 569.

Trichlormolybdic acid,  $\text{MoOCl}_3 \cdot \text{OH} \cdot 7\text{H}_2\text{O}$ , is obtained <sup>1</sup> by the action of fuming hydrochloric acid on the hydroxydichloride.

Cæsium, rubidium, ammonium, and certain organic trichlormolybdates have been prepared.<sup>1</sup>

The *hydroxychlorides*  $\text{Mo}_3\text{Cl}_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Mo}_3\text{Cl}_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , or  $[\text{Mo}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}](\text{OH})_2 \cdot 6\text{H}_2\text{O}$  (see p. 124), are obtained <sup>2</sup> by precipitation with acetic acid, before or after saturation with carbon dioxide respectively, of a solution of molybdenum dichloride in potassium hydroxide.

### MOLYBDENUM AND BROMINE.

**Molybdenum Dibromide,  $\text{MoBr}_2$ ,** is obtained by heating the tribromide, or by strongly heating the metal in bromine vapour.<sup>3</sup> It is a reddish-yellow substance, stable in air, insoluble in water and in acids; in dilute alkalis it is soluble with formation of a hydrate, but by concentrated alkalis it is decomposed. For reasons similar to those applying in the case of the chloride (see p. 123), the formula of the bromide is considered to be  $(\text{Mo}_3\text{Br}_4)\text{Br}_2$ .<sup>4</sup>

Molybdenum dibromide forms a hydroxy-compound  $\text{Mo}_3\text{Br}_4(\text{OH})_2$ , of which the octa- and di-hydrates have also been obtained.<sup>5</sup> In addition, a *fluorobromide*,  $\text{Mo}_3\text{Br}_4\text{F}_2 \cdot 3\text{H}_2\text{O}$ , and *chlorobromides* of molybdenum,  $\text{Mo}_3\text{Cl}_4\text{Br}_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Mo}_3\text{Cl}_4\text{Br}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Mo}_3\text{Cl}_2\text{Br}_4 \cdot 3\text{H}_2\text{O}$ , and the *hydroxychlorobromide*,  $\text{Mo}_3\text{Cl}_4\text{Br} \cdot \text{OH} \cdot 2\text{H}_2\text{O}$ , have been prepared.<sup>6</sup>

**Molybdenum Tribromide,  $\text{MoBr}_3$ ,** is formed when bromine-vapour is passed over moderately heated molybdenum or over a mixture of the dioxide with carbon. The compound sublimes, recondensing to dark green crystals, which tend on heating to decompose into bromine and the dibromide, and which are insoluble in water, dilute acids, or alkalis; they dissolve, however, in concentrated alkalis, the bromide undergoing hydrolysis.<sup>6</sup>

By electrolysis of a solution of molybdic anhydride in hydrobromic acid, using a mercury cathode, a purplish-red solution is obtained, which, on addition of ammonium chloride and subsequent evaporation, deposits <sup>7</sup> deep blood-red crystals of the double bromide  $(\text{NH}_4)_2\text{MoBr}_5 \cdot 2\text{H}_2\text{O}$ .

**Molybdenum Tetrabromide,  $\text{MoBr}_4$ .**—During the preparation of the tribromide, a certain quantity not only of oxybromides (*q.v.*) but also of the tetrabromide is formed, the latter forming black fusible needles soluble in water and hydrolysed by alkalis.<sup>6</sup>

**Oxybromide.** Molybdenum forms an oxybromide,  $\text{MoO}_2\text{Br}_2$ , which may be obtained (*a*) by the interaction of bromine-vapour and heated molybdenum dioxide; (*b*) by heating together potassium bromide, molybdenum trioxide, and boric or phosphoric acid;<sup>6</sup> or (*c*) by interaction in presence of oxygen of molybdenum trioxide and certain

<sup>1</sup> Weinland and Knoll, *Zeitsch. anorg. Chem.*, 1905, 44, 81.

<sup>2</sup> Blomstrand, *J. prakt. Chem.*, 1857, 71, 457.

<sup>3</sup> Blomstrand, *ibid.*, 1859, 77, 89; *ibid.*, 1861, 82, 437; Atterberg, *Jahresber.*, 1872, 25, 260.

<sup>4</sup> Muthmann and Nagel, *Ber.*, 1898, 31, 1836, 2009; Koppel, *Zeitsch. anorg. Chem.*, 1912, 77, 289.

<sup>5</sup> Atterberg, *loc. cit.*

<sup>6</sup> Blomstrand, *loc. cit.*

<sup>7</sup> Rosenheim and Li, *Ber.*, 1923, 56, B, 2228. See also Rosenheim and Braun, *Zeitsch. anorg. Chem.*, 1905, 46, 311.

metallic bromides.<sup>1</sup> It is a stable but deliquescent crystalline substance, having a reddish-yellow colour.

**Dibromomolybdous Acid,  $\text{MoBr}_2 \cdot \text{O} \cdot \text{OH} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , and Tetra-bromomolybdous Acid,  $\text{MoBr}_4 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$ ,** together with salts of ammonium, cæsium, calcium, lithium, magnesium, and rubidium, and certain organic bases, have been described.<sup>2</sup>

#### MOLYBDENUM AND IODINE.

**Molybdenum Di-iodide,  $\text{MoI}_2$ ,** has been prepared<sup>3</sup> by heating the pentachloride to redness in hydrogen iodide as a brown amorphous powder, oxidised on heating and decomposed by boiling water.

The red solutions obtained by dissolving molybdenum sesquioxide or dioxide in aqueous hydrogen iodide were examined by Berzelius,<sup>4</sup> but insufficiently to obtain definite conclusions.

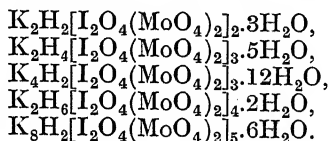
The existence of the compound  $\text{MoI}_4$  has been suggested by Guichard,<sup>5</sup> who obtained black crystals on heating together under pressure hydrogen iodide and molybdenum pentachloride.

The *chloriodides*  $\text{Mo}_3\text{Cl}_4\text{I}_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Mo}_3\text{Cl}_4\text{I}_2 \cdot 6\text{H}_2\text{O}$ , and the *hydroxybromiodide*  $\text{Mo}_3\text{Br}_4\text{I}(\text{OH}) \cdot 4\text{H}_2\text{O}$ , have been described.<sup>6</sup>

**Oxyiodide.**—By heating with potassium iodide a solution of a molybdate in hydrochloric acid, a dark red liquid containing the compound  $\text{MoO}_2\text{I}$  is obtained, with elimination of iodine (see p. 179).<sup>7</sup>

**Iodomolybdic Acid,  $\text{I}_2\text{O}_5 \cdot 2\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ ,** may be obtained<sup>8</sup> by treating with concentrated nitric acid a solution containing iodic and molybdic acids, or by decomposing the barium salt in nitric acid solution by means of sulphuric acid. It yields white microscopic prisms which are extremely soluble in water. Normal salts of the type  $\text{I}_2\text{O}_5 \cdot 2\text{MoO}_3 \cdot \text{R}_2\text{O}$  are precipitated when solutions of the alkali iodates are saturated with molybdenum trioxide, and by double decomposition the corresponding salts of magnesium, calcium, strontium, barium, zinc, nickel, cobalt, copper, and silver have been obtained.

Rosenheim<sup>9</sup> suggests for the free acid the formula  $\text{H}_2[\text{I}_2\text{O}_4(\text{MoO}_4)_2]$ ; but the numerous acid salts, obtainable by interaction of the acid with alkali nitrate solutions, necessitates the use of multiple formulæ. Thus the following potassium salts have been described :



<sup>1</sup> Schultze, *J. prakt. Chem.*, 1883, [2], 281, 434.

<sup>2</sup> Weinland and Knoll, *Zeitsch. anorg. Chem.*, 1905, 44, 81.

<sup>3</sup> Guichard, *Compt. rend.*, 1896, 123, 821.

<sup>4</sup> Berzelius, *Traité de Chimie*, 1847, 4, 379.

<sup>5</sup> Guichard, *Ann. Chim. Phys.*, 1901, [7], 23, 563.

<sup>6</sup> Blomstrand, *J. prakt. Chem.*, 1859, [1], 77, 89; 1861, 82, 423.

<sup>7</sup> Berlin, *ibid.*, 1850, [1], 49, 444.

<sup>8</sup> Chrétien, *Compt. rend.*, 1896, 123, 178; *Ann. Chim. Phys.*, 1898, [7], 15, 358; Blomstrand, *J. prakt. Chem.*, 1889, [2], 40, 305; Rosenheim and Liebknecht, *Annalen*, 1899, 308, 48.

<sup>9</sup> See Abegg, *Handbuch der anorganischen Chemie* (Leipzig, 1921), vol. iv., i., 2nd half, p. 1008.

Complex salts of composition  $4\text{I}_2\text{O}_5 \cdot 3\text{MoO}_3 \cdot 4\text{Ag}_2\text{O}$  and  $4\text{I}_2\text{O}_5 \cdot 3\text{MoO}_3 \cdot 2\text{UO}_3$  have also been described.<sup>1</sup>

**Periodomolybdic Acids,**  $\text{H}_5\text{IO}_6(\text{MoO}_3)$ ,  $\text{H}_5\text{IO}_6(\text{MoO}_3)_4$ , and  $\text{H}_5\text{IO}_6(\text{MoO}_3)_6$ , have been described,<sup>2</sup> and some metallic salts have been prepared.

### MOLYBDENUM AND OXYGEN.

Oxides of molybdenum corresponding to the formulæ  $\text{Mo}_2\text{O}_3$ ,  $\text{MoO}_2$ , and  $\text{MoO}_3$  are known to exist; that represented by the last formula, an acid-forming oxide, has been studied in greatest detail. The intermediate *blue oxide* of molybdenum, obtained by the reduction of the trioxide, is well known, but its composition cannot be considered to be satisfactorily settled; the formula  $\text{Mo}_3\text{O}_8$  is usually ascribed to it.

**Molybdous Oxide.**—The black precipitate obtained by addition of caustic soda to a solution of molybdenum dichloride or dibromide, originally<sup>3</sup> thought to be hydrated molybdous oxide, has been shown<sup>4</sup> actually to be the sesquioxide.

**Molybdenum Sesquioxide,**  $\text{Mo}_2\text{O}_3$ ,<sup>5</sup> is obtained by suitable reduction of the dioxide or trioxide, e.g. by magnesium, zinc, or, preferably, zinc coated with cadmium, and sulphuric or hydrochloric acid,<sup>6</sup> and is apparently known only in the hydrated condition.<sup>7</sup> The hydroxide  $\text{Mo}(\text{OH})_3$ , which may also be obtained electrolytically,<sup>8</sup> was first prepared by Berzelius<sup>9</sup> by the action of zinc and a slight excess of hydrochloric acid upon an aqueous solution of an alkali molybdate; a series of colour changes takes place,<sup>10</sup> the colourless liquid becoming blue, then brown, and finally black. On addition of ammonia the hydroxide separates as a brown powder, which may be freed from traces of zinc salts by washing with very dilute hydrochloric acid.<sup>11</sup> Further, the hydrated sesquioxide is obtained by interaction of potash or soda, and molybdenum dichloride or dibromide, hydrogen being simultaneously evolved,<sup>12</sup> whereas a salt of the same oxide is obtained upon reduction of a solution of molybdic acid in hydrochloric acid by means of copper.<sup>13</sup> The reduction of ammonium molybdate by colloidal palladium, if carried out at ordinary temperatures, yields the tetrahydroxide  $\text{Mo}(\text{OH})_4$ ;<sup>14</sup> if, however, the reduction is effected at  $50^\circ$  to

<sup>1</sup> Chrétien, *loc. cit.*

<sup>2</sup> Rosenheim and Liebknecht, *loc. cit.*; Blomstrand, *Zeitsch. anorg. Chem.*, 1892, **1**, 10.

<sup>3</sup> Blomstrand, *J. prakt. Chem.*, 1859, [1], 77, 91.

<sup>4</sup> Muthmann and Nagel, *Ber.*, 1898, **31**, 1836, 2009.

<sup>5</sup> See Berzelius, *Pogg. Annalen*, 1826, **6**, 369; Blomstrand, *J. prakt. Chem.*, 1857, **71**, 456; Rammelsberg, *ibid.*, 1866, [1], 97, 174.

<sup>6</sup> Chapman and Law, *Analyst*, 1907, **32**, 250; Randall, *Amer. J. Sci.*, 1907, [4], **24**, 313.

<sup>7</sup> Guichard, *Ann. Chim. Phys.*, 1901, [7], **23**, 504; Muthmann, *Annalen*, 1887, **238**, 108; Rammelsberg, *J. prakt. Chem.*, 1866, [1], 97, 174. Cf. Svanberg and Struve, *ibid.*, 1848, **44**, 257.

<sup>8</sup> Wherry and Smith, *J. Amer. Chem. Soc.*, 1907, **29**, 806; Smith, *Ber.*, 1880, **13**, 751; Smith and Hoskinson, *Amer. Chem. J.*, 1885, **7**, 90.

<sup>9</sup> Berzelius, *Pogg. Annalen*, 1826, **6**, 369.

<sup>10</sup> See also Chilesotti, *Zeitsch. Elektrochem.*, 1906, **12**, 146, 197.

<sup>11</sup> Blomstrand, *J. prakt. Chem.*, 1857, **71**, 456.

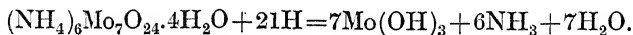
<sup>12</sup> Blomstrand, *ibid.*, 1859, [1], 77, 91; Muthmann and Nagel, *Ber.*, 1898, **31**, 1836, 2009.

<sup>13</sup> Rammelsberg, *Pogg. Annalen*, 1866, **127**, 290. See also Kobell, *J. prakt. Chem.*, 1847, [1], **41**, 158.

<sup>14</sup> Paul and Buttner, *Ber.*, 1915, **48**, 220.



60° C. under a slight pressure, the trihydroxide is obtained as a black sludge :



Molybdenum trihydroxide is an amorphous black substance, becoming reddish brown by slow oxidation in the air. On heating to redness the substance deflagrates, but does not yield the anhydrous oxide. It is insoluble in caustic potash or potassium carbonate solution, but dissolves in excess of ammonium carbonate; its solutions in acids are black in colour.<sup>1</sup>

The salts corresponding to this oxide are dark grey or black, while their solutions have a dark purple or black colour; they are only slightly oxidised in air. The sulphide is an insoluble brown substance, precipitated by hydrogen sulphide or by ammonium sulphide; the chloride, iodide, fluoride, sulphate, and nitrate are soluble. A number of other salts have been prepared.<sup>2</sup>

**Molybdenum Dioxide,  $\text{MoO}_2$ .**—This oxide is produced by a number of reactions involving either the reduction of the trioxide or the oxidation of the sesquioxide. Thus it may be prepared by the action of hydrogen,<sup>3</sup> or of a mixture of carbon monoxide and carbon dioxide,<sup>4</sup> upon molybdic acid<sup>5</sup> or mercurous molybdate; by heating sodium or potassium trimolybdate to redness in hydrogen and washing the residue with water;<sup>6</sup> by heating sodium trimolybdate with zinc and washing the residue with potassium hydroxide solution and then hydrochloric acid;<sup>7</sup> by reduction of ammonium molybdate with colloidal palladium at ordinary temperatures;<sup>8</sup> by heating ammonium molybdate, a mixture of sodium molybdate and ammonium chloride, or a mixture of molybdenum trioxide and ammonium molybdate, and suitably washing the residue with ammonia and then hydrochloric acid;<sup>9</sup> and by electrolysis of fused molybdic anhydride.<sup>10</sup>

Molybdenum dioxide forms<sup>11</sup> violet-blue monoclinic crystals, pseudo-tetragonal,

$$a : b : c = 0.9869 : 1 : 0.5765 ; \beta = 91^\circ 34',$$

of density 6.84.<sup>12</sup> It is more strongly magnetic than the metal.<sup>13</sup> The

<sup>1</sup> Isambert, *Compt. rend.*, 1875, 80, 1087.

<sup>2</sup> See also Gooch and Pulman, *Zeitsch. anorg. Chem.*, 1902, 29, 353; Pisani, *Compt. rend.*, 1864, 59, 301; Rammelsberg, *Zeitsch. anal. Chem.*, 1866, 5, 203.

<sup>3</sup> Liechti and Kempe, *Annalen*, 1873, 169, 344.

<sup>4</sup> Debray, *Compt. rend.*, 1857, 45, 1020.

<sup>5</sup> Unchanged trioxide is removed by Friedheim and Hofmann (*Ber.*, 1902, 35, 791) as oxychloride by heating the oxide in a stream of hydrogen chloride.

<sup>6</sup> Svanberg and Struve, *J. prakt. Chem.*, 1838, 14, 301.

<sup>7</sup> Ullik, *Annalen*, 1867, 144, 227; Muthmann, *ibid.*, 1887, 238, 114.

<sup>8</sup> Paal and Büttner, *Ber.*, 1915, 48, 220.

<sup>9</sup> Svanberg and Struve, *loc. cit.*; Berzelius, *Traité de Chimie*, 1847, 4, 384; Uhrlaub, *Jahresber.*, 1857, 10, 197; Tuttle, *ibid.*, 1857, 10, 194; Berlin, *J. prakt. Chem.*, 1850, [1], 49, 444; Uhrlaub, *Pogg. Annalen*, 1857, 101, 605; Muthmann, *loc. cit.*; Guichard, *Compt. rend.*, 1899, 129, 722; 1900, 131, 998; *Ann. Chim. Phys.*, 1901, [7], 23, 504; *Compt. rend.*, 1906, 143, 744.

<sup>10</sup> Buff, *Annalen*, 1859, 110, 275; Guichard, *Ann. Chim. Phys.*, 1901, [7], 23, 504.

<sup>11</sup> Stevanović, *Zeitsch. Kryst. Min.*, 1903, 37, 254.

<sup>12</sup> Stevanović, *loc. cit.*; Mauro and Panebianco (*Mem. Accad. Lincei*, 1881, [3], 9, 418) give density 6.44, and state that the crystals are ditetragonal (bipyramidal);  $a : c = 1 : 0.5774$ .

<sup>13</sup> Wedekind and Horst, *Ber.*, 1915, 48, 105.

dioxide is insoluble in water, in hydrochloric acid, and in caustic potash solution, but is attacked by nitric acid and by fused potash. It reduces ammoniacal solutions of salts of silver, but not those of mercury or copper.<sup>1</sup>

Reduction of a solution of molybdic acid by means of long digestion with the powdered metal causes the dark blue solution to assume a reddish colour; on addition of ammonia a reddish-brown precipitate is obtained, originally thought to be the hydrate of molybdenum dioxide,<sup>2</sup> but more recently considered<sup>3</sup> to be a hydrate of the oxide  $\text{Mo}_2\text{O}_5$ . The red solution before precipitation contains a salt of this oxide; it is considered probable (Guichard) that the dioxide does not form salts. A similar red solution may be obtained by electrolysis of a sulphuric acid or oxalic acid solution of molybdic acid, or by heating a hydrochloric acid solution of an alkali molybdate with potassium iodide.<sup>4</sup> The hydrate  $\text{MoO}_3 \cdot \text{H}_2\text{O}$ , obtained in each case by precipitation with ammonia, is soluble in water, but is reprecipitated by the addition of salts, thus behaving as a colloid;<sup>5</sup> the aqueous solution upon evaporation yields first a gel, and finally a dark brown *insoluble* hydrate. Though soluble in ammonium carbonate solution, the hydrate in question is insoluble in aqueous caustic potash; in the air it is readily oxidised, giving the blue oxide. The salts obtained by dissolving the freshly precipitated hydroxide in acids (the anhydrous oxide being insoluble) are, when anhydrous, black in colour; when hydrated they are reddish brown; several of these salts are known.<sup>6</sup>

**Molybdenum Oxide (Blue),  $\text{Mo}_3\text{O}_8$  (?) or  $\text{Mo}_5\text{O}_{14}$  (?).**—If a suspension of molybdenum trioxide in water be heated on a water-bath with a large excess of powdered molybdenum, a blue solution is obtained, containing, it is supposed,<sup>7</sup> unpolymerised molecules of the compound  $\text{Mo}_3\text{O}_8$ ; but it is by no means certain either that this formula represents the actual composition of the substance, or that there is but one blue oxide of molybdenum. On addition of certain salts polymerisation is considered (Dumanski) to take place, and the oxide passes to the colloid form.

The blue oxide may be prepared<sup>8</sup> by double decomposition of ammonium dimolybdate and molybdenum chloride, and washing the precipitate first with ammonium chloride solution and then with water; Berzelius accorded the substance the formula  $\text{MoO}_2 \cdot 4\text{MoO}_3$ . Rammelsberg's<sup>9</sup> blue oxide, obtained by interaction of solutions in hydrochloric acid of molybdenum dioxide and trioxide, was given the formula  $\text{MoO}_2 \cdot \text{MoO}_3 \cdot 3\text{H}_2\text{O}$ , while Muthmann's<sup>10</sup> formula was  $\text{MoO}_2 \cdot 2\text{MoO}_3$ , *i.e.*  $\text{Mo}_3\text{O}_8$ . The blue oxide may also be obtained by reduction of ammonium molybdate by means of hydriodic acid, by heating in nitrogen the oxysulphate  $\text{Mo}_2\text{O}(\text{SO}_4)_2$ , or the oxyoxalate  $\text{Mo}_2\text{O}(\text{C}_2\text{O}_4)_2$ ,<sup>11</sup> or by

<sup>1</sup> Smith and Shinn, *Zeitsch. anorg. Chem.*, 1894, 7, 47.

<sup>2</sup> Berzelius, *Traité de Chimie*, 1847, 4, 384.

<sup>3</sup> Klason, *Ber.*, 1901, 34, 148. See also Muthmann, *Annalen*, 1887, 238, 108; Guichard, *Compt. rend.*, 1906, 143, 744.

<sup>4</sup> Péchard, *Compt. rend.*, 1891, 118, 804.

<sup>5</sup> See Freundlich and Leonhardt, *Koll. Chem. Beihefte*, 1915, 7, 172.

<sup>6</sup> See Moissan, *Traité de Chimie*, 1905, 4, 700. See also Skey, *Bull. Soc. chim.*, 1868, 10, 30; Muthmann, *Ber.*, 1887, 20, 989; Krüss, *Annalen*, 1884, 225, 20.

<sup>7</sup> Dumanski, *Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 20.

<sup>8</sup> Berzelius, *Pogg. Annalen*, 1826, 6, 380.

<sup>9</sup> Rammelsberg, *ibid.*, 1866, 127, 281.

<sup>10</sup> Muthmann, *Annalen*, 1887, 238, 108.

<sup>11</sup> Wardlaw and Nicholls, *Trans. Chem. Soc.*, 1925, 127, 1311, 1487.

electrolysis.<sup>1</sup> Guichard<sup>2</sup> considered the blue oxide to be a compound of the formula  $\text{MoO}_2 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$ , while Junius'<sup>3</sup> formula is  $\text{Mo}_7\text{O}_{20}$ .

The blue oxide is best obtained by allowing powdered molybdenum to remain for a long time at ordinary temperatures in contact with an aqueous suspension of the trioxide, filtering, and then digesting with a further quantity of molybdenum. The solution is evaporated *in vacuo*. Cold water used for washing the solid should previously be rendered air-free. Another good method of preparation consists<sup>4</sup> in precipitating in the cold, by means of excess of a solution of hydrated molybdenum tetrachloride, a solution of ammonium molybdate in hydrochloric acid; the precipitate is washed with air-free water in an atmosphere of carbon dioxide, and is dried *in vacuo*.

It is evident, therefore, that the blue oxide may be obtained in a solid state either by precipitation or by evaporation of a solution.<sup>5</sup>

The blue oxide of molybdenum, which can be regarded as a molybdate of molybdenum, is a dark blue substance, of density 3.6 at 18° C., which consists, when obtained by evaporation of a solution, of brilliant vitreous particles, giving the substance a crystalline appearance.<sup>6</sup>

It is a colloid, and is extremely soluble in water, solution taking place slowly in the cold but rapidly at 50° C. A number of salts, *e.g.* sodium or ammonium chloride, without reacting with the blue oxide, considerably reduce its solubility; other salts, *e.g.* sodium or magnesium sulphate, do not exhibit this effect. It is readily dissociated by heat into a mixture of the dioxide and trioxide, and for this reason cannot be dried by heat even *in vacuo*. Oxidation to the trioxide takes place with the dry substance or in solutions slowly at ordinary temperatures but much more rapidly on heating. Its reactions with acids and alkalies point to its formula being probably  $\text{MoO}_2 \cdot 4\text{MoO}_3$ ; with hydrochloric acid the tetrachloride and trioxide are obtained, while with caustic alkali an alkali molybdate and molybdenum dioxide are produced.<sup>7</sup>

**Molybdenum Trioxide,  $\text{MoO}_3$ , or Molybdic Anhydride**, occurs naturally as molybdenite or molybdenum ochre (see p. 111). It is prepared from molybdenite,  $\text{MoS}_2$ , by a process consisting essentially of roasting with or without admixture with sand, and extraction of the resulting mass with ammonia. Separation from copper is effected by the addition of ammonium sulphide, and ammonium molybdate is crystallised from the filtrate. From this compound the trioxide is obtained by

<sup>1</sup> Péchard, *Compt. rend.*, 1892, 114, 1481; Marchetti, *Zeitsch. anorg. Chem.*, 1899, 19, 391. Marchetti's crystalline hydrate was given the formula  $\text{MoO}_2 \cdot 2\text{MoO}_3 \cdot 5\text{H}_2\text{O}$ . See also Maschke, *Zeitsch. anal. Chem.*, 1873, 12, 384.

<sup>2</sup> Guichard, *Ann. Chim. Phys.*, 1901, [7], 23, 557; *Compt. rend.*, 1902, 134, 173.

<sup>3</sup> Junius, *Zeitsch. anorg. Chem.*, 1905, 46, 428. See also Klason, *Ber.*, 1901, 34, 158; Bailhache, *Compt. rend.*, 1901, 133, 1210; Miller and Frank, *J. Amer. Chem. Soc.*, 1903, 25, 919; who have other views on the composition of this oxide.

<sup>4</sup> Guichard, *Ann. Chim. Phys.*, 1901, [7], 23, 520.

<sup>5</sup> For details of the methods available, see Guichard, *loc. cit.*

<sup>6</sup> Guichard, *loc. cit.* Marchetti and Bartalini (*Zeitsch. anorg. Chem.*, 1899, 19, 392) describe the pentahydrate  $\text{Mo}_3\text{O}_8 \cdot 5\text{H}_2\text{O}$  as crystallising in the triclinic system, but Guichard criticises their statement as resting on slender evidence.

<sup>7</sup> The details of these and other reactions are fully described by Guichard, *Ann. Chim. Phys.*, 1901, [7], 23, 536. See also Barbieri, *Atti R. Accad. Lincei*, 1916, [5], 25, i., 775; de Plaza, *Anal. Fis. Quím.*, 1910, 14, 542; *Chemical Abstracts*, 1917, 11, 2864. Suggestions for the use of "molybdenum blue" as a colour have been made by von Kurzer, *Dingl. poly. J.*, 1852, 129, 139; Wagner, *ibid.*, 1878, 205, 386; Hoffmann, *Ber. über die chem. Ind.*, 1875, 1, 1018.

heating in the air.<sup>1</sup> It is preferable, however,<sup>2</sup> to evaporate the solution of ammonium molybdate to dryness with excess of potassium carbonate, extract with water, evaporate again to dryness, and heat the residue with sulphur. After washing with hot water the residual molybdenum sulphide is again treated as already described, and sublimed in platinum vessels in a current of oxygen.<sup>3</sup>

From wulfenite, molybdenum trioxide is prepared by digesting the mineral (previously washed with dilute hydrochloric acid) with concentrated hydrochloric acid; lead still remaining in solution after cooling and filtration is removed by the addition of sulphuric acid, and the filtrate is evaporated to dryness with the addition of a small quantity of nitric acid. The ammonia extract of this mass is then subjected to the method of purification previously described.<sup>4</sup> Another method consists<sup>5</sup> in decomposing the finely powdered mineral by means of concentrated sulphuric acid, diluting to precipitate lead sulphate, and evaporating the filtrate until precipitation of molybdic anhydride occurs.<sup>6</sup>

Molybdic anhydride is a white powder which, on heating, becomes yellow. It melts at 795° C.<sup>7</sup> without decomposition, yielding a reddish-brown liquid,<sup>8</sup> which solidifies on cooling to a yellowish-white fibrous crystalline mass, of density 4.696<sup>9</sup> at 26° C. It sublimes fairly readily in air, rhombic<sup>10</sup> crystals, colourless and transparent, though small, being obtained. Like the dioxide, it is more strongly magnetic than the metal.<sup>11</sup>

Reduction of the trioxide to the dioxide of molybdenum can be effected by means of hydrogen, nitric or nitrous oxides, or sulphur dioxide, while by continued heating in hydrogen a residue of the metal is obtained.<sup>12</sup> The trioxide is slightly soluble in water, yielding a solution which is distinctly metallic to the taste, reddens litmus, and turns turmeric paper brown.<sup>13</sup>

Molybdic anhydride, if unfused, is soluble in acids with the production of a number of complex acids; if previously fused it is, however, insoluble in acids though still soluble in alkalis, yielding the corresponding molybdates.

<sup>1</sup> Berzelius and Wöhler, *Jahresber.*, 1856, 9, 374; Brunner, *ibid.*, 1858, 11, 156.

<sup>2</sup> Svanberg and Struve, *J. prakt. Chem.*, 1848, 44, 257. See also Seubert and Pollard, *Zeitsch. anorg. Chem.*, 1895, 8, 434.

<sup>3</sup> See Ullik, *Annalen*, 1867, 144, 205; Muthmann, *ibid.*, 1887, 238, 117.

<sup>4</sup> Ullik, *loc. cit.*

<sup>5</sup> Elbers, *Annalen*, 1852, 83, 215.

<sup>6</sup> A number of other methods for preparing molybdenum trioxide from minerals have been described. See Dollé, *Pogg. Annalen*, 1852, 85, 450; Christl, *Dingl. poly. J.*, 1851, 124, 398; Buchner and Mahler, *Annalen*, 1853, 83, 320; Wich, *ibid.*, 1861, 118, 43; Wittstein, *Jahresber.*, 1852, 5, 371; Wicke, *Annalen*, 1855, 95, 374; Debray, *Compt. rend.*, 1858, 46, 1098.

<sup>7</sup> Jaeger and Germs, *Zeitsch. anorg. Chem.*, 1921, 119, 145; Grosehuff, *ibid.*, 1908, 58, 113. See also Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

<sup>8</sup> The fused trioxide on electrolysis yields, according to Guichard (*Ann. Chim. Phys.*, 1901, [7], 23, 517), the crystalline dioxide. See also Bleckrode, *Wied. Annalen*, 1878, 3, 161.

<sup>9</sup> Müller, *J. Amer. Chem. Soc.*, 1915, 37, 2046; Schufarik (*Sitzungsber. K. Akad. Wiss. Wien*, 1863, [2], 47, 256) gives density 4.39. See also Carnelley, *loc. cit.* Eggerts (*J. prakt. Chem.*, 1860, 79, 498) gives 4.5 as the density of the sublimed oxide.

<sup>10</sup> Nordenskjöld (*Pogg. Annalen*, 1861, 112, 160) gives a : b : c = 0.3872 : 1 : 0.4792.

<sup>11</sup> Wedekind and Horst, *Ber.*, 1915, 48, 105.

<sup>12</sup> See Guichard, *loc. cit.*; also Ehrenfeld, *J. Amer. Chem. Soc.*, 1895, 3, 81; Blair and Whitfield, *ibid.*, 1896, 17, 747; Schultz, *J. prakt. Chem.*, 1880, [2], 21, 441.

<sup>13</sup> Müller, *Jahresber.*, 1860, 13, 159.

Molybdenum trioxide is an acidic oxide which dissolves in water yielding a solution of molybdic acids, and combines with basic oxides yielding molybdates.

*Hydrates.*—Two definite hydrates of molybdenum trioxide are known to exist,<sup>1</sup> namely,  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  and  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ .

The *dihydrate* is a canary-yellow substance, of density 3.124,<sup>2</sup> which is deposited in a crystalline condition as monoclinic prisms,<sup>2</sup> with

$$a : b : c = 1.0950 : 1 : 1.0664; \beta = 90^\circ 41',$$

when to a 30 per cent. solution of nitric acid there is added with constant stirring an equal volume of a 15 per cent. solution of ammonium paramolybdate, ammonium nitrate added up to a concentration of 10 per cent., and the mixture sown with a few crystals of the dihydrate.<sup>3</sup> The yellow crystalline body which separates from ammonium molybdate-nitric acid reagent is apparently the dihydrate.<sup>4</sup> This hydrate is the most soluble in water of the molybdic acids.<sup>5</sup> The solubility, *i.e.* number of grams of  $\text{MoO}_3$  per 100 grams of solution, in water of the dihydrate is as follows: <sup>6</sup>

Temperature, °C.	20	30	40	50	60	70	75	79
Solubility	0.180	0.257	0.454	0.643	1.076	1.705	1.730	1.740

The solubility curve of the dihydrate cuts that of the monohydrate at 32° C. On heating, two distinct varieties of molybdic acid *monohydrate* are formed; on concentrating the solution of the dihydrate at 40° to 50° C.,  $\alpha$ -molybdic acid *monohydrate* is formed as asbestos-like white needles, retaining their water of crystallisation much more readily than  $\beta$ -molybdic acid *monohydrate*, which is obtained as small white needles, soluble in water, but not regenerating the dihydrate, by heating the dihydrate to 70° C.<sup>7</sup> White  $\alpha$ -molybdic acid is readily obtained <sup>8</sup> by treating methyl molybdate with water. The solubility in water of the monohydrate is as follows: <sup>9</sup>

Temperature, °C.	15	20	30	40	50	60	70	80
Solubility	0.112	0.237	0.293	0.34	0.40	0.47	0.42	0.52

At 60° C. the  $\alpha$ -monohydrate apparently undergoes transformation into the  $\beta$ -monohydrate.<sup>10</sup>

<sup>1</sup> See Hüttig and Kurre, *Zeitsch. anorg. Chem.*, 1923, 126, 167; Burger, *ibid.*, 1922, 121, 240.

<sup>2</sup> de Schulten, *Bull. Soc. franç. Min.*, 1889, 12, 545.

<sup>3</sup> Rosenheim and Berthelm, *Zeitsch. anorg. Chem.*, 1903, 34, 427; Rosenheim and Davidsohn, *ibid.*, 1903, 37, 314; Rosenheim, *ibid.*, 1906, 50, 320.

<sup>4</sup> Graham, *Chem. News*, 1907, 96, 262; Vivier, *Compt. rend.*, 1888, 106, 601; de Schulten, *Bull. Soc. franç. Min.*, 1903, 26, 6; Parmentier, *Compt. rend.*, 1882, 95, 839. See also Wöhler and Engels, *Koll. Chem. Beihefte*, 1910, 1, 454; Mylius, *Ber.*, 1903, 36, 638; Rosenheim, *ibid.*, 1903, 36, 752.

<sup>5</sup> Mylius, *loc. cit.*

<sup>6</sup> Interpolated from values given by Rosenheim and Berthelm, *Zeitsch. anorg. Chem.*, 1903, 34, 430.

<sup>7</sup> Rosenheim and collaborators, *loc. cit.*

<sup>8</sup> Mazzucchelli and Borghi, *Gazzetta*, 1910, 40, ii., 241.

<sup>9</sup> Interpolated from data given by Rosenheim and Davidsohn, *loc. cit.* "Solubility" refers to grams of  $\text{MoO}_3$  per 100 grams of solution.

<sup>10</sup> It is considered that the transformation of the various hydrates of molybdic acid into one another involves the formation of intermediate polymerides.

According to Rosenheim and Bertheim (*loc. cit.*), cryoscopic measurements indicate the existence of octamolybdic acid  $\text{H}_2\text{Mo}_8\text{O}_{25}$ ; according to Mylius (*loc. cit.*), although there is no solid molybdic acid corresponding to telluric acid  $\text{H}_6\text{TeO}_6$ , colourless molybdic acid in aqueous solution corresponds to *allotelluric* acid.

Forsén<sup>1</sup> describes a crystalline compound of composition  $\text{H}_4\text{Mo}_3\text{O}_{11}$ , which he regards as an anhydride of the fundamental hexabasic molybdic acid  $\text{H}_6\text{Mo}_3\text{O}_{12}$  (see p. 137).

A number of complexes of molybdic acid, particularly those with acetylacetone ( $\text{MoO}_2[\text{CH}(\text{COMe})_2]_2$ ), with salicylaldehyde,<sup>2</sup> and with organic acids,<sup>3</sup> have been described, and a number of measurements made of rotatory power.<sup>4</sup>

*Colloidal Molybdic Acid.*—When solutions of sodium molybdate (1 molecule) and hydrochloric acid (4 molecules) are warmed together, or when a solution of molybdic acid dihydrate is evaporated over sulphuric acid under diminished pressure at 20° C., colloidal molybdic acid is formed. From the solution of the hydrosol so obtained, molybdic acid is precipitated by electrolytes.<sup>5</sup> Graham<sup>6</sup> considered that, by dialysis of a solution of sodium molybdate in hydrochloric acid, he obtained colloidal molybdic acid.<sup>7</sup>

Complex molybdic acids are dealt with in connection with the various elements which they contain; for example, for chlormolybdic acids, see p. 126.

**Molybdates.**—Normal molybdates of the type  $\text{R}'_2\text{MoO}_4$  exist in solution but are relatively unstable, and readily form acid salts or complex polymolybdates. Thus dimolybdates,  $\text{R}'_2\text{Mo}_2\text{O}_7$ , can be obtained by fusion of molybdenum trioxide with sodium or potassium nitrate; trimolybdates,  $\text{R}'_2\text{Mo}_3\text{O}_{10}$ , and tetramolybdates,  $\text{R}'_2\text{Mo}_4\text{O}_{13}$ , by heating molybdenum trioxide with an aqueous solution of sodium or potassium carbonate. Even more highly acid salts—for example, octa- and decamolybdates—can be obtained. Solutions of normal molybdates, when treated with hydrochloric acid or nitric acid, yield a precipitate of acid molybdate; this reaction does not, however, take place with sulphuric, acetic, oxalic, or tartaric acids.

Different views have been expressed concerning the relation between the various types of polymolybdates. According to Rosenheim and his collaborators,<sup>8</sup> the tetramolybdates are entirely similar to the meta-

<sup>1</sup> Forsén, *Compt. rend.*, 1921, 172, 215.

<sup>2</sup> Rosenheim and Bertheim, *loc. cit.*

<sup>3</sup> Mazzucchelli, *Atti R. Accad. Lincei*, 1910, [5], 19, ii., 439; Wintgen, *Zeitsch. anorg. Chem.*, 1912, 74, 281; Mazzucchelli, Ranucci, and Sabatini, *Gazzetta*, 1913, 43, ii., 26.

<sup>4</sup> See also Gernez, *Compt. rend.*, 1887, 105, 803; 1889, 108, 942; 1909, 151; 1890, 110, 529; 111, 1365; 1891, 112, 226; 113, 1031; 1892, 114, 480; 1894, 119, 63; Landolt, *Monatsh. preuss. Akad.*, 1887, p. 957; Klason and Köhler, *Ber.*, 1901, 34, 3946; Rosenheim and Itzig, *ibid.*, 1900, 33, 707; Rimbach and Ley, *Zeitsch. physikal. Chem.*, 1922, 100, 393. Meszlényi (*Landw. Versuchs.-Stat.*, 1905, 61, 321) describes a nicotine ammonium molybdate.

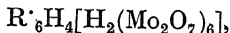
<sup>5</sup> Rosenheim and Davidsohn, *Zeitsch. anorg. Chem.*, 1903, 37, 314; Wöhler and Engels, *Koll. Chem. Beihefte*, 1910, 1, 454.

<sup>6</sup> Graham, *Compt. rend.*, 1864, 59, 174.

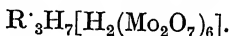
<sup>7</sup> See also Sabanéeff, *Chem. Zentr.*, 1891, i., 10; Ullik, *Annalen*, 1867, 144, 329; 1870, 153, 373. Rosenheim and Davidsohn (*loc. cit.*) consider that the solutions previously prepared by Graham's method, since not precipitated by electrolytes, in all probability contained no colloidal acids.

<sup>8</sup> Rosenheim, Felix, and Pinsker, *Zeitsch. anorg. Chem.*, 1913, 79, 292.

tungstates (see p. 233), and are therefore 12-molybdic acid hydrates of the type



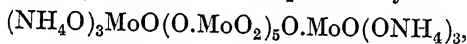
whilst the octamolybdates, which yield hydrogen ions in aqueous solutions, are regarded as hydrogen salts with the same complex anion,



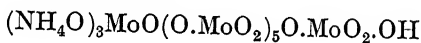
The same authors state that two distinct series of decamolybdates exist, either isomeric or polymeric, one sparingly soluble, and the other readily soluble, in water. The paramolybdates, which have been described under various formulæ,<sup>1</sup> appear to correspond with either  $3R'_2O \cdot 7MoO_3 \cdot aq.$ <sup>2</sup> or  $5R'_2O \cdot 12MoO_3 \cdot aq.$ <sup>3</sup> It has been suggested<sup>4</sup> that these salts are derived from the hypothetical orthomolybdic acid  $H_6MoO_6$  by partial substitution of the group  $Mo_2O_7$  for oxygen, and may be formulated



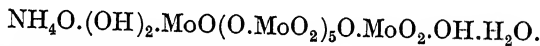
Condensation formulæ have also been suggested.<sup>5</sup> For example, ammonium paramolybdate, which has been obtained in the crystalline form in the anhydrous state, may be expressed by the formula



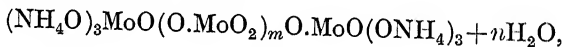
and this view is supported by the preparation of two other ammonium heptamolybdates, of composition



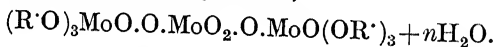
and



When increasing quantities of hydrochloric acid are added to a saturated solution of ammonium paramolybdate, a series of hexabasic polymolybdates, having the general formula<sup>6</sup>



are obtained. Of these, compounds containing 9, 11, 12, and 13 atoms of molybdenum to the molecule have been prepared. All these polymolybdates, with excess of alkali, yield orthomolybdates, which may be regarded as hexabasic trimolybdates,



A series of tetrabasic polymolybdates, containing up to seven molybdic groups, arise by the decomposition of the tridecamolybdates, and compounds containing more than thirteen molybdic groups are not known. The condensation of molybdic acid thus reaches its limit by the formation of tridecamolybdic acid.

<sup>1</sup> See Abegg, *Handbuch der anorganischen Chemie*, vol. iv., pt. 1, 2nd half, p. 577 (Leipzig, 1921).

<sup>2</sup> Lotz, *Annalen*, 1854, 91, 49; Delafontaine, *Arch. Sci. phys. nat.*, 1865, [2], 23, 5; *J. prakt. Chem.*, 1865, 95, 136; Ullik, *Annalen*, 1867, 144, 204, 320.

<sup>3</sup> Junius, *Zeitsch. anorg. Chem.*, 1905, 46, 428; Sand, *Ber.*, 1906, 39, 2038; Sand and Eisenlohr, *Zeitsch. anorg. Chem.*, 1907, 52, 68, 87; Wempe, *ibid.*, 1912, 78, 298.

<sup>4</sup> Copaux, *Compt. rend.*, 1913, 156, 1771.

<sup>5</sup> Posternak, *ibid.*, 1920, 171, 1058, 1213; 1921, 172, 114, 597; Forsén, *ibid.*, 1921, 172, 215, 327.

<sup>6</sup> Posternak, *loc. cit.*

The classification of molybdates into ortho-, meta-, and para-salts is obviously unsatisfactory. There appear to be two main groups of molybdates: <sup>1</sup> (1) the hexabasic polymolybdates, which include among others the ortho- and para-molybdates; and (2) the tetrabasic polymolybdates, including the metamolybdates, which arise from the hexabasic salts by hydrolytic rupture of their chain.

Molybdates combine also with other acidic oxides, forming a series of complex molybdates, the most important of which are probably the phosphomolybdates (see p. 163). The formation of such compounds as diethylmolybdic acid or molybdenum hydroxychloride,  $\text{MoOCl}_2(\text{OH})_2$  (see p. 126), and the sulphate  $\text{MoO}_3 \cdot \text{SO}_3$  (see p. 160), illustrate the behaviour of molybdenum trioxide as a basic oxide.

The absorption spectra of molybdates have been investigated.<sup>2</sup>

Molybdates in aqueous solution are reduced by the common reducing agents, yielding solutions which are reddish, blue, green, or brown, according to the prevailing conditions. Hydrogen sulphide, for instance, produces at first a yellowish colour, changing to green and then blue; finally a brown precipitate of molybdenum sulphide is obtained. For further discussion upon the reactions of molybdates, see p. 177.<sup>3</sup>

**Aluminium Molybdates.**—Simple molybdates of aluminium have not been prepared,<sup>4</sup> but by dissolving aluminium hydroxide in solutions of alkali tri- or para-molybdates, and allowing to crystallise, salts of the type  $3\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot \text{aq.}$  are obtained. These may be represented as derivatives of the alkali aluminates<sup>5</sup> thus:  $\text{R}_3\text{Al}(\text{Mo}_2\text{O}_7)_3 \cdot \text{aq.}$  The following have been described:<sup>6</sup>

$3(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 19\text{H}_2\text{O}$  (or 20 or  $22\text{H}_2\text{O}$ ), white, lustrous, quadratic crystals.

$3\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$ , flat white plates or cubes, stable in air.

$3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 22\text{H}_2\text{O}$ , efflorescent needles.

The barium salt,  $4\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 14\text{H}_2\text{O}$ , is precipitated when a soluble barium salt is added to a solution of the potassium compound. The complex,  $\text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3$ , is very stable, and similar compounds with analogous complexes, containing the sesquioxides of chromium, cobalt, iron, manganese, and nickel, have also been prepared.

**Ammonium Molybdate,**<sup>7</sup>  $(\text{NH}_4)_2\text{MoO}_4$ , is obtained by dissolving ordinary ammonium molybdate or an acid molybdate in ammonia. The crystalline normal salt may be obtained by careful evaporation, or, better, by the addition of alcohol at  $45^\circ \text{C.}$ , in small prisms of density 2.261,<sup>8</sup> which evolve ammonia in the air and are rapidly decomposed by water.<sup>9</sup>

<sup>1</sup> Posternak, *loc. cit.*

<sup>2</sup> von der Pfordten, *Annalen*, 1884, **222**, 157; Krüss, *ibid.*, 1884, **225**, 38; Thalen, *Ann. Chim. Phys.*, 1869, [4], **18**, 202; Copaux, *Compt. rend.*, 1913, **156**, 1771.

<sup>3</sup> See also Annadori, *Atti R. Accad. Lincei*, 1913, [5], **22**, i., 609.

<sup>4</sup> See Struve, *J. prakt. Chem.*, 1854, **61**, 453; Gentile, *ibid.*, 1860, **81**, 411.

<sup>5</sup> Copaux, *Compt. rend.*, 1913, **156**, 1771.

<sup>6</sup> Gentile, *loc. cit.*; Blomstrand, *J. prakt. Chem.*, 1857, **71**, 449; Hall, *J. Amer. Chem. Soc.*, 1907, **29**, 720. See also Marekwald, *Dissertation*, Berlin, 1895; Parmentier, *Compt. rend.*, 1882, **94**, 1713.

<sup>7</sup> The ordinary salt is the paramolybdate.

<sup>8</sup> Marignac, *Arch. Sci. phys. nat.*, 1867, [2], **30**, 30; Koferstein, *Pogg. Annalen*, 1856, **99**, 275; Schröder, *Ber.*, 1878, **11**, 2212.

<sup>9</sup> Svanberg and Struve, *Pogg. Annalen*, 1852, **86**, 594.



**Ammonium Dimolybdate**,  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , exists <sup>1</sup> as monoclinic (prismatic) crystals. A compound  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7 \cdot 3\text{NH}_3$  has been prepared <sup>2</sup> by addition of ammonium hydroxide of medium strength to solid ammonium phosphomolybdate. This substance loses ammonia, yielding the dimolybdate.

**Ammonium Paramolybdate** (*ordinary ammonium molybdate*),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ,<sup>3</sup> is the salt which is obtained by evaporation and crystallisation of a solution of molybdic anhydride in ammonia. It forms large crystals, usually bluish in colour owing to the presence of a lower oxide.<sup>4</sup> The substance is soluble in water; its aqueous solution is stated <sup>5</sup> apparently to contain ions of  $\text{Mo}_6\text{O}_{22}^{8'}$ , formed by hydrolysis of a portion of the  $\text{Mo}_{12}\text{O}_{41}^{10'}$  ions. (It is here assumed that the formula of the solid salt is  $5(\text{NH}_4)_2\text{O} \cdot 12\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ .) The solution is completely reduced by hydrogen in presence of colloidal palladium at ordinary temperatures to molybdenum tetrahydroxide;<sup>6</sup> the reduction goes further if a slight pressure is used and the solution is gently heated, a precipitate of the trihydroxide being formed. The paramolybdate is stable in air; on heating it finally leaves a residue of molybdenum trioxide. From the mother-liquor from which the tetrahydrate forms, a salt,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 12\text{H}_2\text{O}$ , may be obtained.<sup>7</sup> From the nitric acid solution of ammonium molybdate, which <sup>8</sup> contains also acid ammonium molybdate and molybdic acid, there separate on standing hydrates of molybdic anhydride (see p. 134).<sup>9</sup>

**Ammonium Trimolybdate**,  $(\text{NH}_4)_2\text{O} \cdot 3\text{MoO}_3 \cdot \text{H}_2\text{O}$ , is obtained as "warty" crystals from a solution of ordinary ammonium molybdate, by boiling, by allowing to stand for a long time, or by the addition of warm hydrochloric acid.<sup>10</sup> The salt  $(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot 3\text{H}_2\text{O}$  is also said <sup>11</sup> to exist.

**Ammonium Tetramolybdate**,  $(\text{NH}_4)_2\text{O} \cdot 4\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ .<sup>12</sup> This salt is prepared <sup>13</sup> by the action of warm hydrochloric acid or nitric acid upon the ordinary molybdate, and yields transparent triclinic crystals. The solubility at 18° C. of the salt is 3.67 grams in 100 c.c. of water.

**Ammonium Octamolybdate**,  $(\text{NH}_4)_2\text{Mo}_8\text{O}_{25} \cdot 16\text{H}_2\text{O}$ , has been described,<sup>14</sup> but may be regarded <sup>15</sup> as ammonium trihydrogen *tetra*-molybdate,  $\text{NH}_4\text{O} \cdot (\text{OH})_2\text{MoO}(\text{O} \cdot \text{MoO}_2)_3 \cdot \text{OH} \cdot 5\text{H}_2\text{O}$ . This, if left in a

<sup>1</sup> Mauro, *Mem. Accad. Lincei*, 1888, [4], 4, 478.

<sup>2</sup> Sircar, *J. Amer. Chem. Soc.*, 1914, 36, 2372.

<sup>3</sup> Delafontaine, *J. prakt. Chem.*, 1865, 95, 136; Sircar, *loc. cit.* A number of formulae have been suggested. See Klason, *Ber.*, 1901, 34, 153. Junius (*Zeitsch. anorg. Chem.*, 1905, 46, 428), also Sand and Eisenlohr (*ibid.*, 1907, 52, 68), favour the formula  $5(\text{NH}_4)_2\text{O} \cdot 12\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ .

<sup>4</sup> Rath, *Pogg. Annalen*, 1860, 110, 101; Haidinger, *Edin. J. Sci.*, 1897, 1, 100; Marignac, *Arch. Sci. phys. nat.*, 1867, p. 30; Rammelsberg, *Pogg. Annalen*, 1866, 127, 296.

<sup>5</sup> Sand and Eisenlohr, *Zeitsch. anorg. Chem.*, 1907, 52, 68, 87.

<sup>6</sup> Paal and Büttner, *Ber.*, 1915, 48, 220.

<sup>7</sup> Rammelsberg, *Kryst. Chem.*, 1881, 1, 565.

<sup>8</sup> Mylius, *Ber.*, 1903, 36, 638; Rosenheim, *ibid.*, 1903, 36, 752.

<sup>9</sup> See also Hundeshagen, *Zeitsch. anal. Chem.*, 1889, 28, 166; Kern, *Chem. News*, 1878, 37, 98; Jungck, *Jahresber.*, 1876, 29, 271.

<sup>10</sup> Kämmerer, *J. prakt. Chem.*, 1872, [2], 6, 358; Berlin, *ibid.*, 1850, [1], 49, 445; Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.

<sup>11</sup> Jean, *Compt. rend.*, 1874, 78, 1436.

<sup>12</sup> Junius (*Zeitsch. anorg. Chem.*, 1905, 46, 428) describes a hydrate with  $2\frac{1}{2}\text{H}_2\text{O}$ .

<sup>13</sup> Wempe, *loc. cit.*

<sup>14</sup> See also p. 153. See Rosenheim and others, *Zeitsch. anorg. Chem.*, 1913, 79, 292; *ibid.*, 1897, 15, 187; Mylius, *Ber.*, 1903, 36, 638; Berlin, *loc. cit.*

<sup>15</sup> Posternak, *Compt. rend.*, 1921, 172, 114.

vacuum over sulphuric acid, loses  $5\text{H}_2\text{O}$ , and a further molecule of water when heated to  $160^\circ\text{C}$ . Its aqueous solution at  $40^\circ\text{C}$ . yields crystalline needles of the trihydrogen *pentamolybdate*<sup>1</sup>  $\text{NH}_4\text{O} \cdot (\text{OH})_2\text{MoO}(\text{O} \cdot \text{MoO}_2)_4 \cdot \text{OH}$ . Hexa-, hepta-, nona-, undeca-, dodeca-, and tridecamolybdates have also been prepared.<sup>2</sup>

The compound  $\text{NH}_3 \cdot \text{MoO}_2 \cdot (\text{MoO}_3)_2 \cdot 5\text{H}_2\text{O}$  is described<sup>3</sup> as an unstable brown crystalline substance obtained on mixing an aqueous solution of ordinary ammonium molybdate with a solution of molybdenum dioxide in hydrochloric acid.

The *double salts*  $\text{NaNH}_4\text{Mo}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ ,  $2\text{Na}_2\text{O} \cdot 7(\text{NH}_4)_2\text{O} \cdot 21\text{MoO}_3 \cdot 15\text{H}_2\text{O}$ , and  $3\text{Na}_2\text{O} \cdot 7(\text{NH}_4)_2\text{O} \cdot 25\text{MoO}_3 \cdot 30\text{H}_2\text{O}$  have been described.<sup>4</sup>

*Iodomolybdates*.—Three compounds have been described:<sup>5</sup>  $\text{NH}_4\text{IO}_3 \cdot \text{MoO}_3 \cdot \text{H}_2\text{O}$ ;  $(\text{I}_2\text{O}_5 \cdot 2\text{MoO}_3)_4 \cdot 3(\text{NH}_4)_2\text{O} \cdot 6\text{H}_2\text{O}$ ;  $\text{I}_2\text{O}_5 \cdot 2\text{MoO}_3 \cdot (\text{NH}_4)_2\text{O} \cdot \text{H}_2\text{O}$ ; as well as the periodomolybdates,<sup>6</sup>  $(\text{NH}_4)_5\text{IO}_6 \cdot 6\text{MoO}_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)\text{HIO}_6 \cdot \text{MoO}_3$ .

Complex molybdates of ammonium, of the types  $(\text{NH}_4)_3\text{H}_6[\text{R}^{\cdots}(\text{MoO}_4)_6]7\text{H}_2\text{O}$ , where  $\text{R}^{\cdots}$  is Fe, Cr, or Al, and  $(\text{NH}_4)_3\text{H}_7[\text{R}^{\cdots}(\text{MoO}_4)_6]x\text{H}_2\text{O}$ , where  $\text{R}^{\cdots}$  is Co, Mn, or Mg, have been prepared,<sup>7</sup> as also have ammonium rare-earth-molybdates<sup>8</sup> and a *nicotine* ammonium molybdate.<sup>9</sup> The existence has been recorded<sup>10</sup> of double salts of the following formulæ:  $(\text{NH}_4)_2\text{Cu}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ ;  $\text{CuMoO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ ;  $(\text{NH}_4)_2\text{Cd}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ ;  $(\text{NH}_4)_2\text{Ni}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ ;  $(\text{NH}_4)_2\text{Co}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ ; and<sup>11</sup>  $3(\text{NH}_4)_2\text{MoO}_4 \cdot \text{Co}_2(\text{MoO}_4)_3 \cdot 4\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ .

**Barium Molybdates**.—The normal salt  $\text{BaMoO}_4$  is precipitated<sup>12</sup> on addition of aqueous barium chloride to a neutral or ammoniacal solution of ammonium molybdate. By fusion of a mixture containing<sup>13</sup> sodium molybdate (2 parts), barium chloride (6 parts), and sodium chloride (3 parts), barium molybdate may be obtained as a crystalline mass consisting of tetragonal pyramids<sup>14</sup> with  $a:c=1:1.6232$ , and of density<sup>15</sup> 4.648 at  $19.5^\circ\text{C}$ . It is practically insoluble in water, 1 part of the salt dissolving in 17,200 parts of the solvent at  $23^\circ\text{C}$ . It is more readily soluble<sup>16</sup> in presence of ammonium nitrate.

**Barium Paramolybdate**,  $3\text{BaO} \cdot 7\text{MoO}_3 \cdot x\text{H}_2\text{O}$  or  $5\text{BaO} \cdot 12\text{MoO}_3 \cdot y\text{H}_2\text{O}$ , is obtained by drying in air the flocculent precipitate

<sup>1</sup> Described by Rosenheim (*loc. cit.*) as the decamolybdate.

<sup>2</sup> See p. 136. See also Finkener, *Ber.*, 1878, **11**, 1640; Posternak, *Compt. rend.*, 1920, **171**, 1213; 1921, **172**, 114.

<sup>3</sup> Rammelsberg, *Pogg. Annalen*, 1866, **127**, 291.

<sup>4</sup> Mauro, *Gazzetta*, 1884, **11**, 214; Delafontaine, *J. prakt. Chem.*, 1865, **95**, 136.

<sup>5</sup> Chrétien, *Compt. rend.*, 1896, **123**, 178; *Ann. Chim. Phys.*, 1898, **[7]**, **15**, 358.

<sup>6</sup> Blomstrand, *Zeitsch. anorg. Chem.*, 1892, **1**, 10.

<sup>7</sup> Rosenheim and Schwer, *ibid.*, 1914, **89**, 224; Rosenheim, Pieck, and Pinsker, *ibid.*, 1916, **96**, 139. See also Hall, *J. Amer. Chem. Soc.*, 1907, **29**, 692; Struve, *J. prakt. Chem.*, 1854, **61**, 449.

<sup>8</sup> Barbieri (*Atti R. Accad. Lincei*, 1908, **[5]**, **17**, i., 540; 1911, **[5]**, **20**, i., 18; 1913, **[5]**, **22**, i., 781; 1914, **[5]**, **23**, i., 805) describes complex molybdates with cerium, lanthanum, neodymium, praseodymium, samarium, and thorium.

<sup>9</sup> Meszlényi, *Landw. Versuchs.-Stat.*, 1905, **61**, 325.

<sup>10</sup> Briggs, *Trans. Chem. Soc.*, 1904, **85**, 672.

<sup>11</sup> Eliashevitch, *Zeitsch. Kryst. Min.*, 1913, **52**, 630. See also Friedheim and Keller, *Ber.*, 1906, **39**, 4301.

<sup>12</sup> Svanberg and Struve, *J. prakt. Chem.*, 1844, **44**, 257.

<sup>13</sup> Schultze, *Annalen*, 1863, **126**, 49.

<sup>14</sup> Hiortdahl, *Zeitsch. Kryst. Min.*, 1887, **12**, 411.

<sup>15</sup> Clarke and Marsh, *Amer. J. Sci.*, 1877, **[3]**, **14**, 281.

<sup>16</sup> Smith and Bradbury, *Ber.*, 1891, **24**, 2930.

resulting on addition of aqueous barium chloride to a solution of an alkali paramolybdate. If the precipitation takes place at ordinary atmospheric temperature, the composition of the product <sup>1</sup> is represented by  $5\text{BaO} \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$  or  $3\text{BaO} \cdot 7\text{MoO}_3 \cdot 12\text{H}_2\text{O}$ ; precipitation at boiling temperature yields  $5\text{BaO} \cdot 12\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ . By allowing a solution containing barium chloride (1 molecule) and ammonium paramolybdate (10 molecules) to crystallise, the double salt  $3(\text{NH}_4)_2\text{O} \cdot 3\text{BaO} \cdot 14\text{MoO}_3 \cdot 12\text{H}_2\text{O}$  has been obtained.<sup>2</sup>

**Barium Trimolybdate**,  $\text{BaMo}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ , is obtained <sup>3</sup> by the addition of aqueous barium chloride to a solution of an alkali trimolybdate as a white flocculent precipitate which, on drying, becomes horny. The hydrate is slightly soluble in water. On heating to redness it melts, and the liquid on cooling sets to a yellow crystalline mass.

**Barium Tetramolybdate**, **Barium Metamolybdate**,  $\text{BaMo}_4\text{O}_{13} \cdot 5\text{H}_2\text{O}$  or  $\text{Ba}_3\text{H}_4[\text{H}_2(\text{Mo}_2\text{O}_7)_6] \cdot 12\text{H}_2\text{O}$ ,<sup>4</sup> is precipitated when a solution containing barium chloride and sodium octamolybdate is warmed, or when barium octamolybdate is treated with hot water.<sup>5</sup> On heating to  $120^\circ \text{C}$ . the compound loses four-fifths of the water present, which corresponds to the  $12\text{H}_2\text{O}$  in the above constitutional formula. The addition of barium chloride to a solution of sodium tetramolybdate yields the hydrate  $2\text{BaMo}_4\text{O}_{13} \cdot 7\text{H}_2\text{O}$ .<sup>6</sup>

**Barium Octamolybdate**,  $\text{BaMo}_8\text{O}_{25} \cdot 18\text{H}_2\text{O}$ , or **Barium Hydrogen Tetramolybdate**,  $\text{Ba}_3\text{H}_{14}[\text{H}_2(\text{Mo}_2\text{O}_7)_6]_2 \cdot 44\text{H}_2\text{O}$ , may be prepared by double decomposition of barium chloride and concentrated sodium octamolybdate solution;<sup>5</sup> by the action of barium carbonate on a hot solution of molybdic acid dihydrate and evaporation of the resulting liquid; or by treating an aqueous suspension of barium molybdate with hydrochloric acid and allowing the solution to crystallise at room temperature.<sup>4</sup> The salt crystallises in lustrous prisms which are only slightly soluble in cold water, and with warm water yield the tetramolybdate. On heating, the octamolybdate decomposes with loss of water. The compound  $\text{BaMo}_8\text{O}_{25} \cdot 15\text{H}_2\text{O}$  has been obtained as a white amorphous powder, soluble in hot and cold water, by treating a solution of ammonium tetramolybdate with barium chloride.<sup>6</sup>

**Barium Nonamolybdate**,  $\text{BaMo}_9\text{O}_{28} \cdot 4\text{H}_2\text{O}$ , has also been described.<sup>3</sup>

The complex salt  $4\text{BaO} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 15\text{H}_2\text{O}$  or  $\text{Ba}_2\text{H}_5[\text{Cr}(\text{MoO}_4)_6] \cdot 5\text{H}_2\text{O}$  has been obtained.<sup>7</sup>

**Beryllium Molybdate**,  $\text{BeMoO}_4 \cdot 2\text{H}_2\text{O}$ , may be prepared <sup>8</sup> by boiling molecular proportions of beryllium hydroxide and molybdic acid with water; on concentration an oily liquid separates, which gradually solidifies to a mass of needle-shaped crystals of the above composition.

**Bismuth Molybdates**.—Specimens of native bismuth molybdate containing metallic bismuth have been observed in Saxony.<sup>9</sup> The normal salt  $\text{Bi}_2(\text{MoO}_4)_3$  is obtained as a lemon-yellow precipitate on

<sup>1</sup> Junius, *Zeitsch. anorg. Chem.*, 1905, 46, 428. Cf. Wempe, *ibid.*, 1912, 78, 298.

<sup>2</sup> Westphal, *Dissertation*, Berlin, 1895.

<sup>3</sup> Svanberg and Struve, *loc. cit.*

<sup>4</sup> Rosenheim, Felix, and Pinsker, *Zeitsch. anorg. Chem.*, 1913, 79, 292.

<sup>5</sup> Ullik, *Annalen*, 1867, 144, 204, 320.

<sup>6</sup> Wempe, *loc. cit.*

<sup>7</sup> Rosenheim and Schwer, *Zeitsch. anorg. Chem.*, 1914, 89, 224.

<sup>8</sup> Rosenheim and Woge, *ibid.*, 1897, 15, 283.

<sup>9</sup> Schaller, *Bull. U.S. Geol. Survey*, 1916, 610, 10.

adding a solution of bismuth nitrate to potassium molybdate solution. It dissolves in water, 1 part of the salt in 500 parts of water, and also in acids. It crystallises in the tetragonal form with  $a : c = 1 : 1.5636$ , the crystals resembling those of lead molybdate,<sup>1</sup> and having density 6.07 at 15° C. The melting-point of bismuth molybdate is 643° C.<sup>2</sup>

Under certain conditions bismuth may be quantitatively precipitated from a weak nitric acid solution by means of excess of ammonium paramolybdate, in the form of bismuth ammonium molybdate,  $\text{Bi}(\text{NH}_4)(\text{MoO}_4)_2$ .<sup>3</sup>

**Cadmium Molybdates.**—The normal salt  $\text{CdMoO}_4$  is obtained as a heavy white precipitate when a soluble cadmium salt is added to a solution of an alkali molybdate or paramolybdate. The precipitate is readily soluble in mineral acids, ammonium hydroxide, or aqueous potassium cyanide.<sup>4</sup> By fusing together sodium molybdate (2 parts), cadmium chloride (7 parts), and sodium chloride (6 parts), the salt may be obtained as lustrous yellow crystals.<sup>5</sup>

Cadmium paramolybdate cannot be obtained<sup>6</sup> by double decomposition. The salt  $2(\text{NH}_4)_2\text{O} \cdot 3\text{CdO} \cdot 12\text{MoO}_3 \cdot 9\text{H}_2\text{O}$  has been described,<sup>7</sup> as also has the ammonio double salt  $[\text{Cd}(\text{NH}_3)_3](\text{NH}_4)_2(\text{MoO}_4)_2$ .<sup>8</sup>

**Cadmium Octamolybdate**,  $\text{CdMo}_8\text{O}_{25} \cdot 7\text{H}_2\text{O}$ , has been described.<sup>9</sup>

**Cæsium Molybdates.**—The preparation of the normal salt has not been described,<sup>10</sup> but the following polymolybdates have been obtained: <sup>11</sup>  $5\text{Cs}_2\text{O} \cdot 12\text{MoO}_3 \cdot 11\text{H}_2\text{O}$ ;  $2\text{Cs}_2\text{O} \cdot 5\text{MoO}_3 \cdot 5\text{H}_2\text{O}$ ;  $\text{Cs}_2\text{O} \cdot 3\text{MoO}_3 \cdot \text{H}_2\text{O}$ ;  $\text{Cs}_2\text{O} \cdot 4\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ ; and  $\text{Cs}_2\text{O} \cdot 5\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ . By treating the salt last formulated, the pentamolybdate, with concentrated nitric acid, a yellow amorphous powder is obtained which has been described as a hexadecamolybdate,  $\text{Cs}_2\text{O} \cdot 16\text{MoO}_3 \cdot 8\text{H}_2\text{O}$ , but such composition is very doubtful.

**Calcium Molybdate**,  $\text{CaMoO}_4$ , occurs with the tungstate in the mineral powellite (see p. 111). The normal salt is formed as a white precipitate when calcium chloride is added to a hot concentrated solution of sodium molybdate.<sup>12</sup> It may also be obtained, in a manner similar to that used for the barium salt, as white microscopic crystals,<sup>5</sup> tetragonal bipyramidal, with <sup>13</sup>  $a : c = 1 : 1.5457$ .

**Calcium Trimolybdate**,  $\text{CaMo}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ , is prepared by boiling an aqueous suspension of calcium carbonate with excess of molybdic acid,<sup>14</sup> and allowing the filtrate to evaporate. Silky needle-shaped crystals separate which dissolve readily in hot water.

<sup>1</sup> Zambonini, *Gazzetta*, 1920, 50, ii., 128.

<sup>2</sup> A thermal investigation of the system  $\text{PbMoO}_4 - \text{Bi}_2(\text{MoO}_4)_3$  has been made by Zambonini, *loc. cit.*

<sup>3</sup> Riederer, *J. Amer. Chem. Soc.*, 1903, 25, 907; Miller and Frank, *ibid.*, 1903, 25, 919; Miller and Cruser, *ibid.*, 1905, 27, 116.

<sup>4</sup> Smith and Bradbury, *Ber.*, 1891, 24, 2930; Junius, *Zeitsch. anorg. Chem.*, 1905, 46, 428.

<sup>5</sup> Schultze, *Annalen*, 1863, 126, 49.

<sup>6</sup> Junius, *loc. cit.*

<sup>7</sup> Manassewitsch, *Dissertation*, Berne, 1900.

<sup>8</sup> Briggs, *Trans. Chem. Soc.*, 1904, 85, 674.

<sup>9</sup> Wempe, *loc. cit.*

<sup>10</sup> See Retgers, *Zeitsch. physical. Chem.*, 1891, 8, 6.

<sup>11</sup> Rosenheim (*Zeitsch. anorg. Chem.*, 1897, 15, 180), Ephraim and Herschfinkel (*ibid.*, 1909, 64, 263), Wempe (*loc. cit.*), and Muthmann and Nagel (*Ber.*, 1898, 31, 2009), were unable to prepare the trimolybdate.

<sup>12</sup> Ullik, *Annalen*, 1867, 144, 204, 320; Smith and Bradbury, *Ber.*, 1891, 24, 2930.

<sup>13</sup> Hiordahl, *Zeitsch. Kryst. Min.*, 1887, 12, 411.

<sup>14</sup> Ullik, *loc. cit.*

Calcium ammonium paramolybdate, to which the formula  $\text{Ca}(\text{NH}_4)_3\text{H}_5[\text{H}_2(\text{MoO}_4)_6]\cdot 9\text{H}_2\text{O}$  has been given,<sup>1</sup> separates in white needles<sup>2</sup> when ammonium paramolybdate solution is treated with calcium chloride.

**Calcium Tetramolybdate** has not been obtained in the crystalline condition. It remains as a vitreous mass, of composition  $\text{CaMo}_4\text{O}_{13}\cdot 9\text{H}_2\text{O}$ , when the liquid, obtained after boiling an aqueous suspension of calcium carbonate with molybdic acid and filtering, is evaporated rapidly to dryness;<sup>3</sup> if the solution is allowed to stand the trimolybdate (see above) is formed.

**Calcium Octamolybdate**,  $\text{CaMo}_8\text{O}_{25}\cdot 18\text{H}_2\text{O}$ , or  $\text{Ca}_3\text{H}_{14}[\text{H}_2(\text{Mo}_2\text{O}_7)_6]\cdot 22\text{H}_2\text{O}$ ,<sup>4</sup> separates in prismatic crystals when a solution of the normal molybdate in hydrochloric acid (containing 1 molecule  $\text{CaMoO}_4$  to 1.75 molecule  $\text{HCl}$ ) is allowed to evaporate.<sup>3</sup> The crystals dissolve readily in hot water. On heating, water is given up, and the residue fuses. An octamolybdate, of composition  $\text{CaMo}_8\text{O}_{25}\cdot 17\text{H}_2\text{O}$ , separates as an amorphous powder<sup>5</sup> when aqueous solutions containing calcium chloride and sodium tetramolybdate in equivalent proportions are mixed. The precipitate is only slightly soluble in hot water. A dodecamolybdate,  $\text{CaMo}_{12}\text{O}_{37}\cdot 23\text{H}_2\text{O}$ , has also been described.<sup>5</sup>

**Chromium Molybdates.**—Simple molybdates of chromium have not been prepared, but a series of complex salts, analogous to those of aluminium (see p. 137), of the type  $3\text{R}_2\text{O}\cdot \text{Cr}_2\text{O}_3\cdot 12\text{MoO}_3\cdot \text{aq.}$ , may be prepared by the action of chromic hydroxide on solutions of acid molybdates, or by boiling together solutions of chromic salts and paramolybdates and allowing to crystallise.<sup>6</sup> The ammonium salt,  $3(\text{NH}_4)_2\text{O}\cdot \text{Cr}_2\text{O}_3\cdot 12\text{MoO}_3\cdot 20\text{H}_2\text{O}$  (or  $26\text{H}_2\text{O}$ ), and the potassium salt,  $3\text{K}_2\text{O}\cdot \text{Cr}_2\text{O}_3\cdot 12\text{MoO}_3\cdot 20\text{H}_2\text{O}$ , form rose-coloured crystals which are soluble in water, and whose solutions give precipitates with barium, bismuth, caesium, lead, mercurous, rubidium, and silver salts. All these insoluble compounds contain the complex  $\text{Cr}_2\text{O}_3\cdot 12\text{MoO}_3$ , which appears to possess considerable stability. The free chromimolybdic acid  $3\text{H}_2\text{O}\cdot \text{Cr}_2\text{O}_3\cdot 12\text{MoO}_3\cdot \text{aq.}$  is obtained by decomposing the mercurous salt with hydrochloric acid. Two barium salts, of composition  $4\text{BaO}\cdot \text{Cr}_2\text{O}_3\cdot 12\text{MoO}_3\cdot 15\text{H}_2\text{O}$  and  $5\text{BaO}\cdot \text{Cr}_2\text{O}_3\cdot 12\text{MoO}_3\cdot 16\text{H}_2\text{O}$ , have been described.<sup>7</sup>

**Cobalt Molybdates.**—The anhydrous normal salt,  $\text{CoMoO}_4$ , may be prepared by fusing together sodium molybdate, cobalt chloride, and sodium chloride,<sup>8</sup> when it is obtained in greyish-green crystals. It is found with iron in the mineral pateraite. The monohydrate,  $\text{CoMoO}_4\cdot \text{H}_2\text{O}$ , separates in bluish-violet crystals, when solutions containing cobalt chloride and sodium molybdate, or dimolybdate or ammonium paramolybdate, are allowed to crystallise.<sup>9</sup> The crystals are only slightly soluble in hot water, but dissolve readily in acids or ammonium

<sup>1</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>2</sup> Westphal, *Dissertation*, Ber in, 1895.

<sup>3</sup> Ullik, *Annalen*, 1867, 144, 204, 320.

<sup>4</sup> Rosenheim, Felix, and Pinsker, *Zeitsch. anorg. Chem.*, 1913, 79, 292.

<sup>5</sup> Wempe, *ibid.*, 1912, 78, 298.

<sup>6</sup> Struve, *J. prakt. Chem.*, 1854, 61, 453; Marckwald, *Dissertation*, Berlin, 1895; Hall, *J. Amer. Chem. Soc.*, 1907, 29, 720; Rosenheim and Schwer, *Zeitsch. anorg. Chem.*, 1914, 89, 224.

<sup>7</sup> Hall, *loc. cit.*

<sup>8</sup> Schultze, *Annalen*, 1863, 126, 49.

<sup>9</sup> Marckwald, *loc. cit.*; Coloriano, *Bull. Soc. chim.*, 1888, [2], 50, 451.

hydroxide. On heating, the anhydrous salt remains. The ammonio compound  $\text{Co}(\text{NH}_4)_3\text{MoO}_4 \cdot \text{H}_2\text{O}$  has been described.<sup>1</sup>

**Cobalt Dimolybdate,  $2\text{CoMo}_2\text{O}_7 \cdot 11\text{H}_2\text{O}$ .**—The liquor remaining after removal of cobalt molybdate from mixed solutions of cobalt chloride and sodium dimolybdate (see above), when allowed to evaporate in the cold, deposits brown needle-shaped crystals of the above composition. When heated at  $100^\circ \text{C}$ . water is lost and the dihydrate  $\text{CoMo}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  remains.<sup>2</sup>

**Cobalt Trimolybdate,  $\text{CoMo}_3\text{O}_{10} \cdot 10\text{H}_2\text{O}$ ,** separates in rose-coloured needles on evaporating the solution obtained by boiling cobalt carbonate and molybdenum trioxide with water.<sup>3</sup>

A number of *complex* salts have been prepared. By interaction of a cobaltous salt with ammonium paramolybdate, a light red crystalline compound, which may be formulated  $^4 (\text{NH}_4)_3\text{H}_7[\text{Co}(\text{MoO}_4)_6]5\text{H}_2\text{O}$ , has been isolated. Several sodium compounds, probably of the same type, have been described.<sup>2</sup> A series of green cobaltmolybdates, corresponding to the aluminium and chromium salts, has been obtained <sup>5</sup> by oxidation with hydrogen peroxide or ammonium persulphate of an aqueous solution containing cobaltous acetate and ammonium paramolybdate, or by the action of a permolybdate on a cobaltous salt. The ammonium salt,  $3(\text{NH}_4)_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$ , yields green rhombic crystals. The potassium salt,  $3\text{K}_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 15\text{H}_2\text{O}$ , is olive green, and only slightly soluble in water. The following salts have also been prepared:  $2(\text{NH}_4)_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 12\text{H}_2\text{O}$ ;  $3\text{K}_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 11\text{H}_2\text{O}$ ;  $3\text{BaO} \cdot \text{Co}_2\text{O}_3 \cdot 9\text{MoO}_3 \cdot 25\text{H}_2\text{O}$ .

**Copper Molybdates.**—The salt  $4\text{CuO} \cdot 3\text{MoO}_3 \cdot 5\text{H}_2\text{O}$  is a heavy green amorphous substance which is obtained <sup>6</sup> by precipitating a boiling solution of a copper salt with ammonium molybdate. By boiling copper carbonate with excess of molybdic acid and water, fine blue needles of the compound  $\text{CuO} \cdot 3\text{MoO}_3 \cdot 9\text{H}_2\text{O}$  are stated <sup>7</sup> to crystallise on cooling. Copper ammonium molybdates,  $\text{CuO} \cdot (\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot 9\text{H}_2\text{O}$  and  $\text{CuMoO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ , and the compound  $(\text{NH}_4)_2\text{Cu}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ , have been described.<sup>8</sup>

**Ferrous Molybdate.**—The anhydrous normal salt,  $\text{FeMoO}_4$ , is formed by fusing together ferrous chloride, sodium molybdate, and sodium chloride.<sup>9</sup> Molybdates in solution are reduced by the addition of ferrous salts.<sup>10</sup>

**Ferric Molybdate,  $\text{Fe}_2(\text{MoO}_4)_3 \cdot 42\text{H}_2\text{O}$ ,** is obtained as a yellowish-brown precipitate when an aqueous solution of normal sodium molybdate is treated with ferric chloride.<sup>11</sup> If the di- or para-molybdate is so treated, a yellow precipitate, of composition  $\text{Fe}_2\text{O}_3 \cdot 5\text{MoO}_3 \cdot \text{aq.}$ , separates; <sup>12</sup> with the tetramolybdate a pale yellow precipitate, of

<sup>1</sup> Sonnenschein, *J. prakt. Chem.*, 1851, 53, 339.

<sup>2</sup> Marckwald, *loc. cit.*

<sup>3</sup> Ullik, *Annalen*, 1867, 144, 204, 320.

<sup>4</sup> Rosenheim, Pieck, and Pinsker, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>5</sup> Kurnakov, *Chem. Zeit.*, 1900, 14, 113; Friedheim and Keller, *Ber.*, 1906, 39, 4301; Eliashevitch, *Zeitsch. Kryst. Min.*, 1913, 52, 630.

<sup>6</sup> Struve, *Jahresber.*, 1854, p. 350.

<sup>7</sup> Ullik, *Sitzungsber. K. Akad. Wiss. Wien*, 1867, 55, 791.

<sup>8</sup> Struve, *Jahresber.*, 1854, p. 350; Briggs, *Trans. Chem. Soc.*, 1904, 85, 672. See also Rosenheim, Pieck, and Pinsker, *loc. cit.*

<sup>9</sup> Schultze, *Annalen*, 1863, 126, 49.

<sup>10</sup> Struve, *J. prakt. Chem.*, 1854, 61, 453; Steinacker, *Dissertation*, Göttingen, 1861.

<sup>11</sup> Marckwald, *Dissertation*, Berlin, 1895.

<sup>12</sup> Marckwald, *loc. cit.*; Steinacker, *loc. cit.*

composition  $\text{Fe}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 110\text{H}_2\text{O}$ , is obtained on evaporation. Complex salts, of the type  $3\text{R}'_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$  ( $\text{R}' = \text{NH}_4, \text{K}$ ), similar to those of aluminium, chromium, and cobalt, have been described.<sup>1</sup>

**Gold Molybdate (?)**.—A solution of auric chloride, when treated with potassium molybdate, yields a yellow precipitate, soluble in mineral acids.<sup>2</sup>

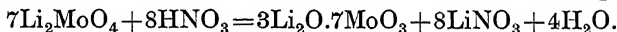
**Indium Molybdate**,  $\text{In}_2(\text{MoO}_4)_3 \cdot 2\text{H}_2\text{O}$ , is obtained<sup>3</sup> as a white voluminous mass when ammonium paramolybdate solution is added to solutions of indium salts.

**Lead Molybdates**.—The normal salt,  $\text{PbMoO}_4$ , occurs in nature as wulfenite (see p. 111). It may be obtained in the crystalline form by fusing together lead chloride and sodium molybdate.<sup>4</sup> The light yellow transparent crystals belong to the tetragonal system,<sup>5</sup> with axial ratio  $a : c = 1 : 1.5771$ , and have density 6.811,<sup>6</sup> hardness 2.75 to 3.0, and melting-point  $1065^\circ \text{C}$ .<sup>7</sup> Lead molybdate is also obtained in the amorphous form by addition of lead nitrate solution to a solution of an alkali molybdate or paramolybdate,<sup>8</sup> when it separates quantitatively as a white precipitate. A *basic* molybdate,  $2\text{PbO} \cdot \text{MoO}_3$ , and an acid molybdate,  $2\text{PbO} \cdot 5\text{MoO}_3$ , have been described.<sup>9</sup>

**Lithium Molybdate**,  $5\text{Li}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , is obtained<sup>10</sup> either by boiling together suitable quantities of lithium carbonate and molybdic anhydride in aqueous suspension, or by extracting with water the mass resulting from the fusion of a mixture containing suitable quantities of lithium carbonate and molybdic anhydride.<sup>11</sup> If allowed to crystallise from hot solutions, the anhydrous salt is obtained in white monoclinic needles.<sup>12</sup> These dissolve readily in water, forming an alkaline solution. If a slight excess of molybdic acid is added to the solution, the sparingly soluble salt,  $2\text{Li}_2\text{O} \cdot 3\text{MoO}_3$ , separates in slender needles.

**Lithium Dimolybdate**,  $\text{Li}_2\text{Mo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ , is obtained in groups of needle-shaped crystals by treating a solution of the normal salt with hydrochloric acid.<sup>12</sup> The dimolybdate readily dissolves in hot water. On heating, it loses one-third of its water at  $120^\circ \text{C}$ ., and the remainder only at red heat.

**Lithium Paramolybdate**,  $3\text{Li}_2\text{O} \cdot 7\text{MoO}_3 \cdot 28\text{H}_2\text{O}$ , is prepared<sup>12</sup> by the action of nitric acid on the normal salt, the reaction being



The salt crystallises in bundles of needles, readily soluble in water.

<sup>1</sup> Struve, *loc. cit.*; Marekwald, *loc. cit.*; Hall, *J. Amer. Chem. Soc.*, 1907, 29, 720.

<sup>2</sup> Richter. See Abegg, *Handbuch der anorganischen Chemie* (Leipzig, 1921), vol. iv., i., 2nd half, p. 613.

<sup>3</sup> Renz, *Ber.*, 1901, 34, 2763.

<sup>4</sup> Manross, *Annalen*, 1852, 82, 358. See also Dittler, *Zeitsch. Kryst. Min.*, 1913, 53, 158; 1914, 54, 332.

<sup>5</sup> Zepharovich, *Sitzungsber. K. Akad. Wiss. Wien*, 1866, 54, 278; Koch, *Zeitsch. Kryst. Min.*, 1882, 6, 389.

<sup>7</sup> Zambonini, *Gazzetta*, 1920, 50, ii., 128.

<sup>6</sup> Manross, *loc. cit.*

<sup>8</sup> Chatard, *Ber.*, 1871, 4, 280; Smith and Bradbury, *ibid.*, 1891, 24, 2930; Junius, *Zeitsch. anorg. Chem.*, 1905, 46, 428.

<sup>9</sup> Jaeger and Germs, *Zeitsch. anorg. Chem.*, 1921, 119, 145; Dittler, *loc. cit.* The systems  $\text{PbO}-\text{PbMoO}_4$ ,  $\text{PbSO}_4-\text{PbMoO}_4$ , and  $\text{PbCrO}_4-\text{PbMoO}_4$ , have been investigated by Jaeger and Germs, *loc. cit.*; and the system  $\text{PbMoO}_4-\text{Bi}_2(\text{MoO}_4)_3$  by Zambonini, *Gazzetta*, 1920, 50, ii., 128.

<sup>10</sup> Rammelsberg, *Pogg. Annalen*, 1866, 128, 311; Delafontaine, *Arch. Sci. phys., nat.*, 1865, 23, 5.

<sup>11</sup> Delafontaine (*loc. cit.*) describes also the salt  $3\text{Li}_2\text{MoO}_4 \cdot 8\text{H}_2\text{O}$ .

<sup>12</sup> Ephraim and Brand, *Zeitsch. anorg. Chem.*, 1909, 64, 258.

**Lithium Trimolybdate**,  $\text{Li}_2\text{O} \cdot 3\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ , is obtained by evaporating a solution of the tetramolybdate, removing any crystals of molybdic acid and concentrating further, when long slender needles separate. When fused and ignited in hydrogen, a dark violet lustrous solid, resembling the alkali tungsten bronzes (see p. 243), is obtained.<sup>1</sup>

**Lithium Tetramolybdate**,  $\text{Li}_2\text{O} \cdot 4\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ , is obtained,<sup>1</sup> by boiling lithium carbonate with a large excess of molybdic acid, as a yellow amorphous mass which gradually becomes hard and brittle. Tetramolybdates, of composition  $\text{Li}_2\text{O} \cdot 3\text{H}_2\text{O} \cdot 16\text{MoO}_3 \cdot 6 \cdot 5\text{H}_2\text{O}$  and  $\text{Li}_2\text{O} \cdot \text{H}_2\text{O} \cdot 8\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ , have been obtained<sup>2</sup> by the action of hydrochloric acid on the normal molybdate. The former yields triclinic crystals, and from its solution a trimolybdate containing 2 or 4  $\text{H}_2\text{O}$  has been obtained.

A *iodomolybdate* of lithium,  $2\text{Li}_2\text{O} \cdot 4\text{MoO}_3 \cdot 2\text{Li}_2\text{O} \cdot 5\text{H}_2\text{O}$ , and *periodomolybdates*,  $\text{Li}_5\text{IO}_6 \cdot 6\text{MoO}_3 \cdot 15\text{H}_2\text{O}$  and  $\text{Li}_5\text{IO}_6 \cdot 6\text{MoO}_3 \cdot 9\text{H}_2\text{O}$ , have been prepared,<sup>3</sup> as well as phospho- and arsenio-molybdates.<sup>4</sup>

**Magnesium Molybdates.**—The **normal molybdate**,  $\text{MgMoO}_4$ , occurs native in belonesite (see p. 111). The *heptahydrate*,  $\text{MgMoO}_4 \cdot 7\text{H}_2\text{O}$ , may be prepared by boiling an aqueous suspension of magnesium oxide with excess of molybdic acid,<sup>5</sup> or by heating a solution containing sodium molybdate and magnesium chloride.<sup>6</sup> In either case, by allowing the clear liquid to crystallise below  $30^\circ \text{C}$ ., thin transparent rhombic prisms, isomorphous with the corresponding sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , separate. The crystals effloresce in the air and dissolve readily in water. If crystallisation occurs above  $30^\circ \text{C}$ ., the *pentahydrate*,  $\text{MgMoO}_4 \cdot 5\text{H}_2\text{O}$ , separates in large lustrous prisms or tablets belonging to the triclinic system, with

$$a : b : c = 0 \cdot 5264 : 1 : 0 \cdot 5732 ; \alpha = 80^\circ 43', \beta = 98^\circ 52', \gamma = 107^\circ 28' ;$$

and isomorphous with magnesium chromate,  $\text{MgCrO}_4 \cdot 5\text{H}_2\text{O}$ , and with copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .<sup>7</sup> The crystals have density 2.208, and are readily soluble in water. On heating, the pentahydrate loses  $3\text{H}_2\text{O}$  at  $120^\circ \text{C}$ ., while at red heat both the penta- and hepta-hydrates yield the anhydrous salt,  $\text{MgMoO}_4$ , without fusion or decomposition.

By evaporation of solutions containing equimolecular quantities of magnesium molybdate and an alkali molybdate, *double salts* of the type  $\text{R}_2\text{Mg}(\text{MoO}_4)_2 \cdot 2\text{H}_2\text{O}$  have been prepared;<sup>8</sup> whilst from a solution containing equivalent proportions of magnesium molybdate and potassium chromate, a double salt, similar in form and behaviour to the above, and of composition  $\text{K}_2\text{Mg}(\text{CrO}_4)(\text{MoO}_4) \cdot 2\text{H}_2\text{O}$ , may be obtained.<sup>8</sup>

**Magnesium Paramolybdate**,  $3\text{MgO} \cdot 7\text{MoO}_3 \cdot 20\text{H}_2\text{O}$ , may be prepared<sup>8</sup> by the action of nitric acid on magnesium molybdate in solution; upon evaporation, small transparent prisms are obtained.

<sup>1</sup> Ephraim and Brand, *loc. cit.*

<sup>2</sup> Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.

<sup>3</sup> Chrétien, *Compt. rend.*, 1896, 123, 178; *Ann. Chim. Phys.*, 1898, [7], 15, 358.

<sup>4</sup> Pufahl, *Ber.*, 1884, 17, 217.

<sup>5</sup> Struve, *J. prakt. Chem.*, 1854, 61, 453; Ullik, *Annalen*, 1867, 144, 204, 320.

<sup>6</sup> Westphal, *Dissertation*, Berlin, 1895.

<sup>7</sup> Struve, *loc. cit.*; Delafontaine, *Arch. Sci. phys. nat.*, 1867, [2], 30, 232; Wyrnboff, *Bull. Soc. min. de France*, 1889, 12, 60.

<sup>8</sup> Ullik, *loc. cit.*; also *Annalen*, 1870, 153, 373.



The salt is readily soluble in water. It is stable at atmospheric temperature, and becomes anhydrous on heating.

From a solution containing ammonium paramolybdate (1 molecule) and magnesium nitrate (2 molecules) colourless crystals have been obtained,<sup>1</sup> which may be formulated  $^2$   $(\text{NH}_4)_3\text{Mg}\cdot\text{H}_5[\text{H}_2(\text{MoO}_4)_6]\cdot 6\text{H}_2\text{O}$ .

**Magnesium Trimolybdate**,  $\text{MgMo}_3\text{O}_{10}\cdot 10\text{H}_2\text{O}$ , is obtained<sup>3</sup> by drying in air the needle-shaped crystals, which separate on evaporating a solution of the normal molybdate containing excess of acetic acid.

**Magnesium Tetramolybdate** has not been prepared.<sup>4</sup> The octamolybdate  $\text{MgMo}_8\text{O}_{25}\cdot 20\text{H}_2\text{O}$ <sup>3</sup> or  $\text{MgO}\cdot\text{H}_2\text{O}\cdot 8\text{MoO}_3\cdot 20\text{H}_2\text{O}$ <sup>4</sup> has been described, as also has the compound  $\text{MgMo}_{16}\text{O}_{49}\cdot 30\text{H}_2\text{O}$ .<sup>3</sup>

**Manganese Molybdate**,  $\text{MnMoO}_4$ , is obtained in the anhydrous condition by fusing together sodium molybdate, manganous chloride, and sodium chloride.<sup>5</sup> By treating normal or acid molybdate solutions with manganous salts,<sup>6</sup> the manganese molybdate may be separated in the hydrated condition. Several hydrates have been described, but the existence of the *monohydrate* only appears to be established. This is a white crystalline powder.

*Polymolybdates* of manganese have not been obtained. A large number of complex salts have been described,<sup>7</sup> on the composition of which, however, differing views have been expressed.

**Mercurous Molybdates.**—When a neutral solution of an alkali molybdate is treated with mercurous nitrate, the molybdenum is completely precipitated in the form of a mercurous molybdate of uncertain composition. The precipitate on ignition is converted to molybdic anhydride, so that the reaction may be used (see p. 179) for the estimation of molybdenum. The *normal salt*,  $\text{Hg}_2\text{O}\cdot\text{MoO}_3$ , may be obtained<sup>8</sup> in the form of golden-yellow needles by treating a solution of alkali trimolybdate with mercurous nitrate, and boiling the resulting yellowish-white precipitate with the mother-liquid. If the precipitate is immediately filtered and washed until all volatile matter is removed, the *dimolybdate*,  $\text{Hg}_2\text{O}\cdot 2\text{MoO}_3$ , remains.

**Mercuric Molybdates** of definite composition have not been prepared.<sup>9</sup>

**Molybdenum Molybdate**, molybdenum blue, the blue oxide of molybdenum, has already been described (see p. 131).

**Nickel Molybdates.**—The normal salt,  $\text{NiMoO}_4$ , is obtained in the anhydrous condition by fusion of nickel chloride with sodium molybdate and sodium chloride.<sup>10</sup> In the hydrated condition it may be obtained by crystallising from mixed solutions of nickel chloride and sodium molybdate;<sup>11</sup> in the cold, a green pentahydrate,  $\text{NiMoO}_4\cdot 5\text{H}_2\text{O}$ ,

<sup>1</sup> Westphal, *Dissertation*, Berlin, 1895.

<sup>2</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>3</sup> Ullik, *Annalen*, 1867, 144, 204, 320.

<sup>4</sup> Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.

<sup>5</sup> Schultze, *Annalen*, 1863, 126, 49.

<sup>6</sup> Struve, *J. prakt. Chem.*, 1854, 61, 453.; Coloriano, *Bull. Soc. chim.*, 1888, [2], 50, 451; Marckwald, *Dissertation*, Berlin, 1895.

<sup>7</sup> Marckwald, *loc. cit.*; Rosenheim, *loc. cit.*; Struve, *loc. cit.*; Péchard, *Compt. rend.*, 1897, 125, 31.; Rosenheim and Itzig, *Zeitsch. anorg. Chem.*, 1898, 16, 81.; Friedheim and Samelson, *ibid.*, 1900, 24, 67.; Hall, *J. Amer. Chem. Soc.*, 1907, 29, 720.

<sup>8</sup> Struve, *loc. cit.*

<sup>9</sup> See Hirzel, *Annalen*, 1852, 84, 261.

<sup>10</sup> Schultze, *ibid.*, 1863, 126, 49.

<sup>11</sup> Marckwald, *loc. cit.*

separates; whilst from a hot solution, crystals of composition  $3\text{NiMoO}_4 \cdot 2\text{H}_2\text{O}$  are obtained. From mixed solutions of nickel chloride and sodium dimolybdate, yellow crystals of the dihydrate,  $\text{NiMoO}_4 \cdot 2\text{H}_2\text{O}$ , are deposited; when sodium paramolybdate is employed, green crystals of the trimolybdate,  $\text{NiO} \cdot 3\text{MoO}_3 \cdot 18\text{H}_2\text{O}$ , separate.

Complex molybdates, of composition <sup>1</sup>  $5(\text{NH}_4)_2\text{O} \cdot 3\text{NiO} \cdot 16\text{MoO}_3 \cdot 16\text{H}_2\text{O}$  and  $5\text{K}_2\text{O} \cdot 3\text{NiO} \cdot 16\text{MoO}_3 \cdot 21\text{H}_2\text{O}$ , may be obtained by treating hot solutions of ammonium or potassium paramolybdate with nickel sulphate. The potassium salt is probably more correctly formulated <sup>2</sup> as  $2\text{K}_2\text{O} \cdot \text{NiO} \cdot 6\text{MoO}_3 \cdot 8\text{H}_2\text{O}$ , and appears to contain 3 molecules of water of constitution, so that it may be considered to be a complex salt of the type  $\text{K}_4\text{H}_6[\text{Ni}(\text{MoO}_4)_6] \cdot 5\text{H}_2\text{O}$ . Corresponding salts of silver and barium have been obtained by double decomposition.<sup>2</sup> The sodium salt,  $\text{Na}_2\text{O} \cdot 2\text{NiO} \cdot 6\text{MoO}_3 \cdot 17\text{H}_2\text{O}$ , obtained <sup>3</sup> by treating a hot solution of sodium paramolybdate with a nickel salt, may be formulated <sup>2</sup> as a salt of the same type, thus:  $\text{Na}_2\text{NiH}_6[\text{Ni}(\text{MoO}_4)_6] \cdot 14\text{H}_2\text{O}$ .

Complex salts containing tetravalent nickel of the type  $3\text{R}'_2\text{O} \cdot \text{NiO}_2 \cdot 9\text{MoO}_3 \cdot n\text{H}_2\text{O}$ , may be obtained <sup>1</sup> by treating a mixed solution of potassium or ammonium paramolybdate and nickel sulphate with a persulphate. The potassium salt forms as a fine dark brown crystalline precipitate, whilst the ammonium salt yields purple crystals. A barium salt,  $3\text{BaO} \cdot \text{NiO}_2 \cdot 9\text{MoO}_3 \cdot 12\text{H}_2\text{O}$ , is formed as a brown precipitate on the addition of barium chloride to a solution of the ammonium salt.

**Platinum Molybdates.**—Simple molybdates of platinum have not been obtained. A number of complex platinomolybdates of the alkali metals, containing tetravalent platinum, have been described,<sup>4</sup> but their existence as compounds has not been confirmed.

**Potassium Molybdate,  $\text{K}_2\text{MoO}_4$ ,** is obtained <sup>5</sup> by the addition of potassium trimolybdate, in small quantities at a time, to alcoholic caustic potash solution; the oily layer which separates is washed with alcohol and crystallised over sulphuric acid. Another method consists <sup>6</sup> in fusing together suitable proportions of molybdenum trioxide or ammonium molybdate and potassium carbonate, taking up the mass with water and crystallising over sulphuric acid. The solid melts at  $919^\circ \text{C}$ .<sup>7</sup> and appears to exist in four different modifications (*cf.* Sodium Molybdate, p. 152), since it exhibits *three* transformation points, namely,  $327^\circ \text{C}$ .,  $454^\circ \text{C}$ ., and  $479^\circ \text{C}$ .<sup>8</sup> The salt is deliquescent and absorbs carbon dioxide from the air. It dissolves readily in water, 100 grams of the saturated solution at  $25^\circ \text{C}$ . containing <sup>9</sup> 64.86 grams  $\text{K}_2\text{MoO}_4$ . It is insoluble in alcohol.

**Potassium Dimolybdate,  $\text{K}_2\text{Mo}_2\text{O}_7$ ,** is formed by fusion of suitable quantities of  $\text{K}_2\text{CO}_3$  and  $\text{MoO}_3$ , but is unstable; the aqueous

<sup>1</sup> Hall, *J. Amer. Chem. Soc.*, 1907, 29, 720.

<sup>2</sup> Barbieri, *Atti R. Accad. Lincei*, 1914, [5], 23, ii, 357.

<sup>3</sup> Marcwald, *loc. cit.*

<sup>4</sup> Gibbs, *Amer. J. Sci.*, 1877, [3], 14, 62; *Ber.*, 1877, 10, 1385; *Amer. Chem. J.*, 1895, 17, 73.

<sup>5</sup> Svanberg and Struve, *J. prakt. Chem.*, 1848, [1], 44, 265; Péchard, *Compt. rend.*, 1893, 117, 788; Parmentier, *ibid.*, 1882, 94, 213; Delafontaine, *J. prakt. Chem.*, 1865, [1], 95, 136.

<sup>6</sup> Ullik, *Annalen*, 1869, 144, 208.

<sup>7</sup> van Klooster, *Zeitsch. anorg. Chem.*, 1914, 85, 49.

<sup>8</sup> See also Hüttner and Tammann, *ibid.*, 1905, 43, 215; Amadori, *Atti R. Accad. Lincei*, 1913, [5], 22, i, 453, 609; 1914, [5], 23, i, 707, 800.

<sup>9</sup> Amadori, *loc. cit.*

extract of the fused mass yields large crystals which immediately begin to decompose.<sup>1</sup>

The salt melts at 484° C., apparently without transformation.<sup>2</sup>

**Potassium Paramolybdate**,  $K_6Mo_7O_{24} \cdot 4H_2O$ ,<sup>3</sup> is readily obtained (1) by evaporating a solution of molybdenum trioxide in excess of aqueous potassium carbonate, redissolving the dry residue in the smallest possible quantity of hot water, and crystallising; <sup>4</sup> or (2) by precipitating such a solution by means of concentrated nitric acid or sulphuric acid.<sup>5</sup> The milky liquid obtained by adding sufficient acid to redissolve the precipitate at first formed slowly deposits crystals of the salt, which cannot be purified by recrystallisation owing to the ease with which they decompose, yielding the trimolybdate and normal molybdate.

Potassium paramolybdate crystallises in prisms isomorphous with the corresponding ammonium salt (p. 138).<sup>6</sup> The fused anhydrous salt is but slightly soluble in water.

**Potassium Trimolybdate**,  $K_2Mo_3O_{10} \cdot 3H_2O$  (? $2H_2O$  ?), is often produced, either spontaneously or by the action of water, from other molybdates (see above). It may be prepared <sup>8</sup> by fusing one molecular proportion of potassium carbonate with two of molybdic anhydride; the aqueous extract of the fused mass deposits crystals of the trimolybdate. Another method of preparation consists <sup>9</sup> in saturating boiling potassium carbonate solution with molybdenum trioxide, filtering, and allowing the solution to stand. The salt forms silky needles which become anhydrous at 100° C., and are less soluble in water than the corresponding sodium salt.<sup>10</sup>

**Potassium Tetramolybdate**, **Potassium Metamolybdate**,  $K_2Mo_4O_{13} \cdot 7H_2O$  or  $K_6H_4[H_2(Mo_2O_7)_6] \cdot 18H_2O$ , is obtained<sup>11</sup> as a heavy microcrystalline precipitate on warming a solution of sodium octamolybdate with potassium chloride. It forms transparent prismatic crystals, slightly soluble in water. On boiling with water it yields the trimolybdate. The tetramolybdate is also formed in solution when molybdic acid (4 molecules) is treated with potassium carbonate (1 molecule); the reacting mixture must be kept cool or the trimolybdate is obtained.<sup>12</sup>

**Potassium Octamolybdate**, **Potassium Hydrogen Tetramolybdate**,  $K_2Mo_8O_{25} \cdot 13H_2O$  or  $K_3H_7[H_2(Mo_2O_7)_6] \cdot 15H_2O$  (see p. 136), has been prepared <sup>8</sup> by allowing to crystallise a solution of trimolybdate to which molybdic anhydride has been added until a precipitate begins to form; by double decomposition of hot solutions of ammonium tetramolybdate and potassium sulphate; <sup>13</sup> or by saturating a solution of the

<sup>1</sup> Ullik, *Annalen*, 1869, 144, 208.

<sup>2</sup> Amadori, *Atti R. Accad. Lincei*, 1913, [5], 22, i., 609.

<sup>3</sup> Cf. Svanberg and Struve (*loc. cit.*), Delafontaine (*loc. cit.*),  $K_8Mo_9O_{31} \cdot 6H_2O$ .

<sup>4</sup> Delafontaine, *Pogg. Annalen*, 1866, 127, 293.

<sup>5</sup> Svanberg and Struve, *J. prakt. Chem.*, 1848, [1], 44, 257.

<sup>6</sup> Marignac, *Pogg. Annalen*, 1866, 127, 293.

<sup>7</sup> Junius, *Zeitsch. anorg. Chem.*, 1905, 46, 428.

<sup>8</sup> Ullik, *loc. cit.*

<sup>9</sup> Svanberg and Struve, *loc. cit.*; Struve, *J. prakt. Chem.*, 1854, 61, 453.

<sup>10</sup> See also Forsén, *Compt. rend.*, 1921, 172, 215.

<sup>11</sup> Rosenheim, Felix, and Pinsker, *Zeitsch. anorg. Chem.*, 1913, 79, 292.

<sup>12</sup> Rosenheim, *ibid.*, 1897, 15, 180. See also Wempe, *ibid.*, 1912, 78, 298.

<sup>13</sup> Wempe, *loc. cit.*

tetramolybdate with sulphur dioxide.<sup>1</sup> The salt is decomposed by water.

**Potassium Decamolybdate**,  $K_2Mo_{10}O_{31} \cdot 9H_2O$  and  $15H_2O$ , has been prepared.<sup>2</sup>

Thiomolybdates, phosphomolybdates, arseniomolybdates, etc., are dealt with under the corresponding acids.

A number of **iodomolybdates** (see p. 128) and **periodomolybdates** of potassium are known.<sup>3</sup>

A large number of complex potassium chromi-molybdates, alumi-molybdates, ferri-molybdates, etc., have been described<sup>4</sup> (see pp. 137, 142).

**Molybdates of the Rare Earth Metals.**<sup>5</sup>—Salts of the type  $M_2(MoO_4)_3$  have been described. The cerous salt is obtained<sup>6</sup> as yellow crystals by fusing together anhydrous cerous chloride and sodium molybdate. The density of the molten salt is <sup>7</sup> 4.56. The crystals are similar to those of lead and bismuth molybdates,<sup>8</sup> as also are those of "didymium" molybdate.<sup>5</sup>

A number of *complex molybdates* have been prepared containing the rare earth elements of the cerium group. They have the general formula  $(NH_4)_6M^{+++}_2Mo_{11}O_{48} \cdot 24H_2O$ , and form a series of isomorphous salts crystallising in the triclinic system.<sup>9</sup> They may be considered as double salts of the paramolybdate series.<sup>10</sup> A well-defined series of complex *cerimolybdates*, analogous to the complex salts of thorium and zirconium, and derived from an acid of the type  $4H_2O.CeO_3.12MoO_3.aq.$ , has been prepared.<sup>11</sup> The salts do not give the reactions for  $Ce^{+++}$ ; for example, they are unattacked by hydrogen peroxide, so that the cerium appears to be present in a complex ion, and the formula  $H_8[Ce(Mo_2O_7)_6]aq.$  has been suggested. The neutral ammonium salt,  $(NH_4)_8[Ce(Mo_2O_7)_6] \cdot 8H_2O$ , is obtained as yellow crystals by treating an aqueous solution of ammonium paramolybdate with a solution of cerium ammonium nitrate. By the action of dilute sulphuric acid on a solution of the normal salt, the acid salt,  $(NH_4)_6H_2[Ce(Mo_2O_7)_6] \cdot 10H_2O$ , has been prepared, and by double decomposition the silver salt,  $Ag_8[Ce(Mo_2O_7)_6]$ , may be isolated.

**Rhodium Molybdates.**—Complex rhodimolybdates, of the type  $3R_2O.Rh_2O_3.12MoO_3 \cdot nH_2O$ , and analogous to the corresponding compounds of aluminium, iron, chromium, and cobalt, have been described.<sup>12</sup> The ammonium salt,  $3(NH_4)_2O.Rh_2O_3.12MoO_3.20H_2O$ , crystallises in

<sup>1</sup> Rosenheim, *loc. cit.*; Rosenheim, Felix, and Pinsker, *loc. cit.*; Asch, *Dissertation*, Berlin, 1902.

<sup>2</sup> Rosenheim and others, *loc. cit.*

<sup>3</sup> Blomstrand, *J. prakt. Chem.*, 1889, [2], 40, 305; Chrétien, *loc. cit.*; Blomstrand, *Zeitsch. anorg. Chem.*, 1892, 1, 10; Friedheim and Keller, *Ber.*, 1906, 39, 4301.

<sup>4</sup> Struve, *J. prakt. Chem.*, 1854, 61, 449; Hall, *J. Amer. Chem. Soc.*, 1907, 29, 692; Eliashevitch, *Zeitsch. Kryst. Min.*, 1913, 52, 630; Barbieri, *Atti R. Accad. Lincei*, 1913, [5], 22, i, 781; Rosenheim and Schwer, *Zeitsch. anorg. Chem.*, 1914, 89, 224.

<sup>5</sup> See this series, Vol. IV., 1921, p. 265.

<sup>6</sup> Didier, *Compt. rend.*, 1886, 102, 823.

<sup>7</sup> Cossa, *ibid.*, 1886, 102, 1315; La Valle, *Gazzetta*, 1886, 16, 334.

<sup>8</sup> Zambonini, *Gazzetta*, 1920, 50, ii, 128.

<sup>9</sup> Barbieri, *Atti R. Accad. Lincei*, 1908, [5], 17, i, 540; 1911, [5], 20, i, 18; Billows, *Zeitsch. Kryst. Min.*, 1912, 50, 500. For crystallographic data, see this series, Vol. IV., 1921, p. 265.

<sup>10</sup> Rosenheim and Schwer, *Zeitsch. anorg. Chem.*, 1914, 89, 224.

<sup>11</sup> Barbieri, *Atti R. Accad. Lincei*, 1914, [5], 23, i, 805.

<sup>12</sup> Barbieri, *ibid.*, 1914, [5], 23, i, 334.

minute yellow laminæ. The potassium salt is similar in appearance and composition.

A series of **rubidium molybdates** has been prepared.<sup>1</sup>

**Rubidium Molybdate**,  $\text{Rb}_2\text{MoO}_4$ , is prepared by dissolving molybdenum trioxide in a warm solution of rubidium hydroxide; after evaporation, and washing of the deliquescent mass with alcohol, white crusts of the normal salt remain.

**Rubidium Dimolybdate**,  $\text{Rb}_2\text{O} \cdot 2\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ , crystallises in readily soluble prisms or plates from solutions containing some nitric acid.

**Rubidium Paramolybdate**,  $\text{Rb}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , is one of the products obtained by boiling rubidium molybdate with molybdic acid and crystallising the solution. A salt with  $14\text{H}_2\text{O}$  has also been noted.

**Rubidium Trimolybdate**,  $\text{Rb}_2\text{Mo}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ <sup>2</sup> or  $3\text{H}_2\text{O}$ ,<sup>3</sup> is prepared by fusing rubidium carbonate with excess of molybdenum trioxide and extracting with boiling water. Brilliant hexagonal crystals, soluble in water, are deposited. A hydrate, of the approximate composition  $\text{Rb}_2\text{O} \cdot 3\text{MoO}_3 \cdot 6 \cdot 5\text{H}_2\text{O}$ , is a product of the decomposition of the paramolybdate by hot water.

**Rubidium Tetramolybdates**.—Including the octamolybdates, which are regarded as acid tetramolybdates, a number are known, corresponding to the formulæ  $\text{Rb}_2\text{O} \cdot 4\text{MoO}_3$ ,  $\text{Rb}_2\text{O} \cdot 4\text{MoO}_3 \cdot 0 \cdot 5\text{H}_2\text{O}$ ,  $\text{Rb}_2\text{O} \cdot 4\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ , and  $\text{Rb}_2\text{O} \cdot \text{H}_2\text{O} \cdot 8\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ ; the salt  $\text{Rb}_2\text{O} \cdot \text{MoO}_3 \cdot \text{Rb}_2\text{O} \cdot 3\text{MoO}_3 \cdot 5\text{H}_2\text{O}$  is regarded as a double salt.<sup>3</sup>

Other rubidium molybdates are: <sup>1</sup>  $4\text{Rb}_2\text{O} \cdot 5\text{MoO}_3 \cdot 12\text{H}_2\text{O}$ ;  $5\text{Rb}_2\text{O} \cdot 7\text{MoO}_3 \cdot 6 \cdot 5\text{H}_2\text{O}$ ;  $3\text{Rb}_2\text{O} \cdot 8\text{MoO}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{Rb}_2\text{O} \cdot 11\text{MoO}_3 \cdot 5 \cdot 5\text{H}_2\text{O}$ ;  $\text{Rb}_2\text{O} \cdot 13\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ ;  $\text{Rb}_2\text{O} \cdot 18\text{MoO}_3$ .

**Silver Molybdates**.—There have been described normal silver molybdate, an acid salt  $2\text{Ag}_2\text{O} \cdot 5\text{MoO}_3$ , and a tetramolybdate  $\text{Ag}_2\text{O} \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$ , besides the ammoniacal salt  $\text{Ag}_2\text{MoO}_4 \cdot 4\text{NH}_3$  (which is prepared<sup>4</sup> either by absorption of ammonia by the dry salt, or by evaporating an ammoniacal solution of the molybdate with lime and ammonium chloride) and<sup>5</sup> a cerimolybdate.

**Normal Silver Molybdate**,  $\text{Ag}_2\text{MoO}_4$ , is obtained<sup>6</sup> as a yellowish-white flocculent precipitate by double decomposition of solutions of silver nitrate and normal potassium molybdate; it may be obtained<sup>7</sup> in colourless crystals<sup>8</sup> by slowly evaporating strongly ammoniacal solutions of silver nitrate and molybdic acid. It is readily fusible, is slightly soluble in water, and is soluble in nitric acid, potassium cyanide, and ammonia.<sup>9</sup>

The *acid molybdate*  $2\text{Ag}_2\text{O} \cdot 5\text{MoO}_3$  is said<sup>10</sup> to be obtained by a similar double decomposition.

<sup>1</sup> Ephraim and Herschinkel, *Zeitsch. anorg. Chem.*, 1909, 64, 263; Wempe, *ibid.*, 1912, 78, 298.

<sup>2</sup> Delafontaine, *Arch. Sci. phys. nat.*, 1865, 23, 5.

<sup>4</sup> Widmann, *Bull. Soc. chim.*, 1873, [2], 20, 64.

<sup>5</sup> Barbieri, *Atti R. Accad. Lincei*, 1913, [5], 22, i., 781.

<sup>6</sup> Svanberg and Struve, *Jahresber.*, 1847, p. 412; Smith and Bradbury, *Ber.*, 1891, 24, 2934.

<sup>7</sup> Debray, *Compt. rend.*, 1868, 66, 735.

<sup>8</sup> The crystal structure of silver molybdate has been shown to be similar to that of spinels and magnetite. See Wyckoff, *J. Amer. Chem. Soc.*, 1922, 44, 1994.

<sup>9</sup> See also Krutwig, *Ber.*, 1881, 14, 304; Wöhler and Rautenberg, *Annalen*, 1860, 114, 119; Muthmann, *Ber.*, 1887, 20, 984.

<sup>10</sup> Svanberg and Struve, *loc. cit.*

<sup>3</sup> Wempe, *loc. cit.*

The *tetramolybdate*  $\text{Ag}_2\text{O} \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$  is known.<sup>1</sup>

An *iodomolybdate* of silver,  $4\text{Ag}_2\text{O} \cdot 3\text{MoO}_3 \cdot 4\text{I}_2\text{O}_5$ , has been described.<sup>2</sup>

**Sodium Molybdates.**—A number of compounds of sodium hydroxide with molybdic acid exist.

**Sodium Molybdate,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ,** may be prepared by fusing together requisite proportions of sodium carbonate and molybdenum trioxide and crystallising from the aqueous extract,<sup>3</sup> or by neutralising a saturated aqueous solution of the trioxide or an acid molybdate by

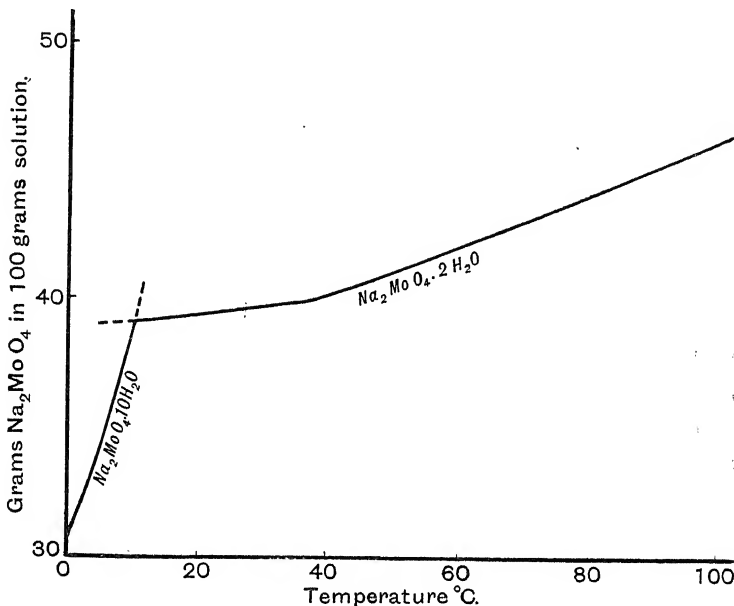


FIG. 3.—Solubility of sodium molybdate.

warm sodium carbonate solution.<sup>4</sup> On evaporating in carbon dioxide-free air, lustrous plates, or rhombohedra are obtained. The solubility<sup>5</sup> is as follows :<sup>6</sup>

Temperature, ° C.	0	4	6	9	10	15.5	18	32	51.5	100
Solubility .	30.63	33.83	35.48	38.16	39.28	39.27	39.40	39.82	41.27	45.57

the solid phase above 10° C. being  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , and below 10° C.,  $\text{Na}_2\text{MoO}_4 \cdot 10\text{H}_2\text{O}$ , as is shown in fig. 3. The solubility curve resembles that of sodium tungstate (see p. 227). The decahydrate is obtained<sup>7</sup> in large striated (efflorescent) prisms, similar to the sulphate, when a solution is crystallised below 6° C. On gently heating, the crystals yield the dihydrate.

<sup>1</sup> Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.

<sup>2</sup> Chrétien, *loc. cit.*

<sup>3</sup> Svanberg and Struve, *J. prakt. Chem.*, 1848, 44, 257.

<sup>4</sup> Delafontaine, *ibid.*, 1865, 95, 140; Ullik, *Annalen*, 1867, 144, 211.

<sup>5</sup> Grams of  $\text{Na}_2\text{MoO}_4$  per 100 grams of solution.

<sup>6</sup> Funk, *Ber.*, 1900, 33, 3697.

<sup>7</sup> Delafontaine, *loc. cit.*; Ullik, *loc. cit.*; Gentile, *J. prakt. Chem.*, 1865, 95, 140.

Further heating yields the anhydrous salt, which melts at  $687^{\circ}\text{C}.$ <sup>1</sup> and apparently exists in four different modifications, since three transformation points have been observed. These have been determined as follows :

Authority.	Transformation Points, $^{\circ}\text{C}.$					
	By Heating.			By Cooling.		
Amadori <sup>2</sup> . . .	444	592	634	410	580	616
van Klooster <sup>3</sup> . . .	445	592	640			
Boeke <sup>4</sup> . . . . .	431	587	619			

**Sodium Dimolybdate**,  $\text{Na}_2\text{Mo}_2\text{O}_7$ , is formed when suitable quantities of sodium carbonate or nitrate and molybdenum trioxide are fused together, and the mass washed free of carbonate or nitrate by cold water.<sup>5</sup> The small crystals so obtained are only slightly soluble in either cold or hot water. From such a solution in hot water, prisms of the monohydrate,  $\text{Na}_2\text{Mo}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , are deposited.<sup>6</sup>

**Sodium Paramolybdate**,  $\text{Na}_6\text{Mo}_7\text{O}_{24} \cdot 22\text{H}_2\text{O}$ , obtained by dissolving molybdenum trioxide in a slight excess of sodium carbonate,<sup>7</sup> by precipitating a saturated solution of molybdic anhydride in sodium carbonate solution by means of nitric acid,<sup>8</sup> or by interaction of molybdic anhydride and borax solution,<sup>9</sup> forms large efflorescent glassy crystals which readily fuse in their water of crystallisation and become anhydrous at  $130^{\circ}\text{C}.$  It is slightly soluble in cold water, but quite readily so in hot water. The constitution of paramolybdates is discussed on p. 136.

**Sodium Trimolybdate**,  $\text{Na}_2\text{Mo}_3\text{O}_{10} \cdot (?)7\text{H}_2\text{O}$ ,<sup>10</sup> crystallises<sup>11</sup> from a saturated solution of molybdenum trioxide in sodium carbonate,<sup>12</sup> or from such a solution treated with a suitable excess of nitric acid;<sup>13</sup> or it may be obtained by the addition of a large excess of acetic acid to a solution of the paramolybdate.<sup>14</sup> The trimolybdate yields fine needles which at  $100^{\circ}\text{C}.$  lose  $6\text{H}_2\text{O}$ ; it is rather more soluble in hot than in cold water.<sup>15</sup>

<sup>1</sup> van Klooster, *Zeitsch. anorg. Chem.*, 1914, 85, 49. Boeke (*ibid.*, 1906, 50, 355) states  $692^{\circ}\text{C}.$

<sup>2</sup> Amadori, *Atti R. Accad. Lincei*, 1914, [5], 23, i., 707.

<sup>3</sup> van Klooster, *loc. cit.*

<sup>4</sup> Boeke, *loc. cit.* Also Groschuff, *Zeitsch. anorg. Chem.*, 1908, 58, 113.

<sup>5</sup> Ullik, *Annalen*, 1867, 144, 211.

<sup>6</sup> Svanberg and Struve, *loc. cit.* Gentele (*loc. cit.*) affirms the existence of a heptahydrate, but this has not been confirmed.

<sup>7</sup> Ullik, *Annalen*, 1867, 144, 218.

<sup>8</sup> Zenker, *J. prakt. Chem.*, 1852, 58, 490.

<sup>9</sup> Mauro, *Gazzetta*, 1884, 11, 214. See also Junius (*Zeitsch. anorg. Chem.*, 1905, 46, 428), who describes a compound  $5\text{Na}_2\text{O} \cdot 12\text{MoO}_3 \cdot 36\text{H}_2\text{O}$ .

<sup>10</sup> Wempe's formula (see below) is  $\text{Na}_2\text{Mo}_3\text{O}_{10} \cdot 6$  or  $9\text{H}_2\text{O}$ .

<sup>11</sup> Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.

<sup>12</sup> This solution also contains a tetramolybdate.

<sup>13</sup> Svanberg and Struve, *loc. cit.*

<sup>14</sup> Ullik, *loc. cit.*

<sup>15</sup> 100 parts  $\text{H}_2\text{O}$  at  $20^{\circ}\text{C}.$  dissolve 3.878 parts; at  $100^{\circ}\text{C}.$  about 13.7 parts.

**Sodium Tetramolybdate**,  $\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ , can be obtained from the mother-liquor from the crystallisation of the trimolybdate (*q.v.*). Hydrates with  $5.5$  and  $6\text{H}_2\text{O}$ ,<sup>1</sup> as well as the anhydrous salt, have been described,<sup>2</sup> but the constitution of the salt usually obtained has been stated<sup>3</sup> to be  $\text{Na}_6\text{H}_4[\text{H}_2(\text{Mo}_2\text{O}_7)_6]21\text{H}_2\text{O}$ . The salt yields yellow microscopic crystals. The acid salt  $\text{NaHMo}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$  has been prepared<sup>4</sup> by interaction of four molecular proportions of "normal" sodium molybdate with seven of hydrochloric acid. Two octamolybdates,  $\text{Na}_2\text{Mo}_8\text{O}_{25} \cdot 4\text{H}_2\text{O}$ , or  $\text{Na}_2\text{Mo}_8\text{O}_{25} \cdot 17\text{H}_2\text{O}$ , and  $\text{NaHMo}_8\text{O}_{25} \cdot 4\text{H}_2\text{O}$ ,<sup>5</sup> which may also be considered as hydrogen tetramolybdates (see p. 136), have been prepared.

A *pentamolybdate*,  $\text{NaHMo}_5\text{O}_{16} \cdot 10\text{H}_2\text{O}$ ,<sup>6</sup> and *decamolybdates*, of composition  $\text{Na}_2\text{Mo}_{10}\text{O}_{31} \cdot 12\text{H}_2\text{O}$ ,<sup>7</sup> or possibly  $\text{Na}_2\text{Mo}_{10}\text{O}_{31} \cdot 6\text{H}_2\text{O}$ , and  $\text{Na}_2\text{Mo}_{10}\text{O}_{31} \cdot 22\text{H}_2\text{O}$ ,<sup>8</sup> have been described.

The *double salt*  $2\text{Na}_2\text{MoO}_4 \cdot \text{K}_2\text{MoO}_4 \cdot 14\text{H}_2\text{O}$  is known,<sup>8</sup> as also are the salts  $\text{LiNa}_3(\text{MoO}_4)_2 \cdot 6\text{H}_2\text{O}$ <sup>9</sup> and  $\text{K}_2\text{Na}_4(\text{MoO}_4)_3 \cdot 14\text{H}_2\text{O}$ .<sup>10</sup>

For thiomolybdates, phosphomolybdates, etc., see pp. 160, 165, 168.

**Sodium Iodomolybdate**,  $\text{Na}_2\text{O} \cdot 2\text{MoO}_3 \cdot \text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , has been prepared,<sup>11</sup> as have also the **sodium periodomolybdates**,  $\text{Na}_5(\text{MoO}_3)_6\text{IO}_6 \cdot 17\text{H}_2\text{O}$ ,  $\text{Na}_5\text{MoO}_3\text{IO}_6$ , and  $\text{NaH}_2(\text{NH}_4)_2\text{MoO}_3\text{IO}_6 \cdot 8\text{H}_2\text{O}$ .<sup>12</sup>

**Stannous and stannic molybdates** have not been isolated. The addition of alkali molybdates to solutions of stannous salts causes precipitation of a blue oxide containing tin, possibly as stannic molybdate.

A complex salt, of composition<sup>13</sup>  $(\text{NH}_4)_8[\text{Sn}(\text{Mo}_2\text{O}_7)_6] \cdot 20\text{H}_2\text{O}$ , is obtained as a microcrystalline white powder by the action of ammonium paramolybdate on ammonium chlorostannate.

**Strontium Molybdate**,  $\text{SrMoO}_4$ , is prepared by fusing together sodium molybdate (1 part), strontium chloride (2 parts), and sodium chloride (2 parts). It crystallises in white quadratic pyramids,<sup>14</sup> with axial ratio<sup>15</sup>

$$a : c = 1 : 1.5738,$$

and of density<sup>16</sup>  $4.145$  at  $21^\circ \text{C}$ . It is only slightly soluble in water, 1 part of the salt dissolving<sup>17</sup> in 9600 parts of water.

Higher molybdates of strontium are not known with certainty. An octamolybdate, of composition<sup>18</sup>  $\text{SrMo}_8\text{O}_{25} \cdot 7\text{H}_2\text{O}$ , has, however, been

<sup>1</sup> Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.

<sup>2</sup> Ullik, *Annalen*, 1867, 144, 324; 1870, 153, 372.

<sup>3</sup> Rosenheim, Felix, and Pinsker, *Zeitsch. anorg. Chem.*, 1913, 79, 292.

<sup>4</sup> See Ullik, *Annalen*, 1870, 153, 372; Zepharovich, *Sitzungsber. K. Akad. Wiss. Wien*, 1868, 58, 112.

<sup>5</sup> Ullik, *loc. cit.*; Rosenheim, Felix, and Pinsker, *loc. cit.*

<sup>6</sup> Ullik, *loc. cit.*; Zepharovich, *loc. cit.*

<sup>7</sup> Ullik, *loc. cit.*

<sup>8</sup> Ullik, *Annalen*, 1867, 144, 211; Marignac, *Arch. Sci. phys. nat.*, 1865, 23, 8.

<sup>9</sup> Ditrigonal pyramidal;  $a : c = 1 : 0.8957$ ;  $\alpha = 100^\circ 36'$  (Traube, *Zeitsch. Kryst. Min.*, 1896, 26, 644).

<sup>10</sup> Dihexagonal bipyramidal;  $a : c = 1 : 1.2839$ ; Marignac, *Pogg. Annalen*, 1866, 127, 293.

<sup>11</sup> Chrétien, *Compt. rend.*, 1896, 123, 178; *Ann. Chim. Phys.*, 1898, [7], 15, 358.

<sup>12</sup> Chrétien, *loc. cit.*; Blomstrand, *J. prakt. Chem.*, 1889, [2], 40, 305; Copaux, *Compt. rend.*, 1913, 156, 1771.

<sup>13</sup> Rosenheim, Pieck, and Pinsker, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>14</sup> See Hiortdahl, *Zeitsch. Kryst. Min.*, 1887, 12, 411.

<sup>15</sup> Schultze, *Annalen*, 1863, 126, 49.

<sup>16</sup> Clarke and Marsh, *Amer. J. Sci.*, 1877, [3], 14, 281.

<sup>17</sup> Smith and Bradbury, *Ber.*, 1891, 24, 2930.

<sup>18</sup> Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.



described. It is obtained as needle-shaped crystals by treating a solution of ammonium tetramolybdate with strontium chloride and allowing the mixture to evaporate.

**Thallous Molybdate**,  $\text{Ti}_2\text{MoO}_4$ , may be prepared by boiling molybdenum trioxide with thallous hydroxide or carbonate solution; <sup>1</sup> by the addition of a thallous salt to a solution of a normal molybdate; <sup>2</sup> or by heating the fluoroxymolybdate,  $\text{MoO}_2\text{F}_2 \cdot 2\text{TlF}$ , to redness in air. <sup>3</sup> The salt is slightly soluble in cold water, more soluble in hot water, and from the hot solution it crystallises in pearly leaflets. It dissolves in alkali hydroxides and in aqueous hydrofluoric acid. On strongly heating it melts to a yellow liquid.

**Thallous Paramolybdate**,  $5\text{Ti}_2\text{O} \cdot 12\text{MoO}_3$ , <sup>4</sup> is obtained as a yellow microcrystalline precipitate when excess of hot thallous sulphate solution is added to a hot solution of sodium paramolybdate. The salt is slightly soluble in water, readily soluble in mineral acids and in alkalis. On heating it deepens in colour, and melts at red heat to a dark brown liquid. Thallous paramolybdate is interesting in that it is unusual to obtain paramolybdates in the anhydrous condition.

**Thallous Tetramolybdate**,  $\text{Ti}_2\text{O} \cdot 4\text{MoO}_3 \cdot \text{H}_2\text{O}$ , is prepared <sup>5</sup> by double decomposition of ammonium tetramolybdate and thallous sulphate.

**Thorium Molybdate**,  $\text{Th}(\text{MoO}_4)_2$ , is obtained by fusing partly dehydrated thorium chloride with excess of anhydrous sodium molybdate. It yields tetragonal crystals, <sup>6</sup> with axial ratio

$$a : c = 1 : 0.73565,$$

and density 4.92 at 7.5° C. The crystals exhibit mutual miscibility in the solid state with cerous molybdate (see p. 149).

A series of complex *thoromolybdates*, derived from an acid of the type  $\text{H}_8[\text{Th}(\text{Mo}_2\text{O}_7)_6]$ , has been prepared. <sup>7</sup> The normal ammonium salt,  $(\text{NH}_4)_8[\text{Th}(\text{Mo}_2\text{O}_7)_6] \cdot 8\text{H}_2\text{O}$ , forms as a white precipitate on the addition of thorium sulphate to a concentrated solution of ammonium paramolybdate. The thoromolybdate dissolves in nitric acid, and the solution is almost completely precipitated by silver nitrate. The solution in nitric or hydrochloric acid, when treated with a concentrated solution of an ammonium salt, yields ammonium hydrogen thoromolybdate,  $(\text{NH}_4)_6\text{H}_2[\text{Th}(\text{Mo}_2\text{O}_7)_6] \cdot 11\text{H}_2\text{O}$ . The corresponding sodium salts,  $\text{Na}_8[\text{Th}(\text{Mo}_2\text{O}_7)_6] \cdot 15\text{H}_2\text{O}$  and  $\text{Na}_6\text{H}_2[\text{Th}(\text{Mo}_2\text{O}_7)_6] \cdot 17\text{H}_2\text{O}$ , are similarly prepared. Silver thoromolybdate,  $\text{Ag}_8[\text{Th}(\text{Mo}_2\text{O}_7)_6]$ , is a white powder. The solutions of the ammonium and sodium salts also yield precipitates on the addition of magnesium or zinc salts.

**Uranium Molybdates**.—Uranyl molybdate,  $\text{UO}_2\text{MoO}_4$ , is obtained <sup>8</sup> as a white amorphous precipitate when ammonium molybdate is added to uranyl nitrate solution in the dark. It is reduced to uranous molybdate,  $\text{U}(\text{MoO}_4)_2$ , becoming green by the action of ethyl or methyl alcohol or acetic acid, and dissolves in mineral acids with a yellowish-

<sup>1</sup> Delafontaine, *Arch. Sci. phys. nat.*, 1867, [2], 30, 232; Flemming, *Jenaische Zeitsch.*, 1868, 4, 33.

<sup>2</sup> Oettinger, *Zeitsch. Chem.*, 1864, p. 440; Flemming, *loc. cit.*

<sup>3</sup> Mauro, *Atti R. Accad. Lincei*, 1893, [5], 2, ii., 382.

<sup>4</sup> Junius, *Zeitsch. anorg. Chem.*, 1905, 46, 428; *Dissertation*, Berlin, 1905.

<sup>5</sup> Wempe, *loc. cit.*

<sup>6</sup> Zambonini, *Atti R. Accad. Lincei*, 1923, [5], 32, i., 518.

<sup>7</sup> Barbieri, *ibid.*, 1913, [5], 22, i., 781.

<sup>8</sup> Lancien, *Compt. rend.*, 1907, 144, 1434.

green fluorescence. When exposed to sunlight, uranyl molybdate gradually becomes golden-yellow in colour, and the product is no longer soluble in nitric acid, nor is it reduced by alcohol. The salt is strongly radioactive.

The *paramolybdate*,  $3\text{UO}_3 \cdot 7\text{MoO}_3$ , is obtained as a curdy precipitate by the addition of uranyl nitrate to ammonium paramolybdate solution. On drying it yields a yellow amorphous powder, which dissolves in acids with a yellowish-green fluorescence. It is hydrolysed by water to uranyl hydroxide and molybdic acid.<sup>1</sup>

**Uranyl Octamolybdate**,  $\text{UO}_3 \cdot 8\text{MoO}_3 \cdot 13\text{H}_2\text{O}$ , is obtained by treating the paramolybdate with nitric acid in sunlight, and allowing the solution to evaporate, when it crystallises in prismatic needles.<sup>1</sup>

**Zinc Molybdates.**—The anhydrous normal salt,  $\text{ZnMoO}_4$ , is obtained as microcrystalline needles by fusing together <sup>2</sup> sodium molybdate (2 parts), zinc chloride (3 parts), and sodium chloride (6 parts), and extracting with hot water. On addition of a zinc salt to a solution of an alkali molybdate, an amorphous precipitate of zinc molybdate is formed, which on prolonged treatment with hot water assumes the crystalline form and yields fine white transparent needles of the monohydrate  $\text{ZnMoO}_4 \cdot \text{H}_2\text{O}$ . The crystals are slightly soluble in water, readily soluble in acids. On heating, the compound loses water, but is not completely dehydrated at  $100^\circ \text{C}$ .<sup>3</sup> An ammoniated compound,  $\text{Zn}(\text{NH}_3)_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ , has been described.<sup>4</sup>

Zinc paramolybdate has not been prepared. A solution of ammonium paramolybdate, when treated with a zinc salt, yields a white, insoluble double salt, of composition <sup>5</sup>  $2(\text{NH}_4)_2\text{O} \cdot \text{ZnO} \cdot 7\text{MoO}_3 \cdot 15\text{H}_2\text{O}$ .

**Zinc Trimolybdate**,  $\text{ZnO} \cdot 3\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ , may be prepared by boiling an aqueous suspension of zinc carbonate with excess of molybdic anhydride,<sup>6</sup> filtering, and allowing to crystallise, or by evaporating a mixed solution of sodium tetramolybdate and zinc sulphate.<sup>5</sup> The salt crystallises in needles which readily dissolve in hot water. On heating, the trimolybdate loses  $4\text{H}_2\text{O}$  at  $120^\circ \text{C}$ ., and becomes anhydrous at  $140^\circ \text{C}$ .

**Zinc Tetramolybdate**,  $\text{ZnMo}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$ , is obtained as a vitreous mass in a similar manner to the corresponding calcium salt (see p. 142), which it resembles in properties.

**Zinc Octamolybdate**,  $\text{ZnMo}_8\text{O}_{25} \cdot 15\text{H}_2\text{O}$ , is obtained <sup>7</sup> as transparent crystals by allowing a solution containing equivalent quantities of ammonium tetramolybdate and zinc sulphate to crystallise.

**Zirconium Molybdate**,  $\text{Zr}(\text{MoO}_4)_2 \cdot 21\text{H}_2\text{O}$ , is obtained by precipitation of ammonium paramolybdate solution with zirconium sulphate.<sup>8</sup>

Complex compounds of the type  $2\text{R}'_2\text{O} \cdot 2\text{H}_2\text{O} \cdot \text{ZrO}_2 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$  ( $\text{R}' = \text{K}, \text{NH}_4$ .) have been described.<sup>9</sup>

<sup>1</sup> See Abegg, *Handbuch der anorganischen Chemie* (Leipzig, 1921), vol. iv., 1, ii., p. 947.

<sup>2</sup> Schultze, *Annalen*, 1863, 126, 49.

<sup>3</sup> Coloriano, *Bull. Soc. chim.*, 1888, [2], 50, 451; Manassewitsch, *Dissertation*, Berne, 1900.

<sup>4</sup> Sonnenschein, *J. prakt. Chem.*, 1851, 53, 339.

<sup>5</sup> Ullik, *Annalen*, 1867, 144, 204, 320.

<sup>6</sup> Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 298.

<sup>7</sup> Kulka, *Dissertation*, Berne, 1902.

<sup>8</sup> Péchard, *Compt. rend.*, 1893, 117, 788.

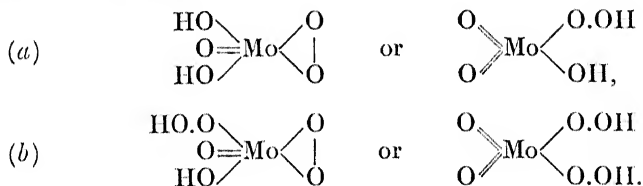
<sup>9</sup> Manassewitsch, *loc. cit.*

## PERMOLYBDIC ACID AND PERMOLYBDATES.

If a solution of a molybdate be treated in acid solution with hydrogen peroxide, oxidation to permolybdic acid takes place, the solution becoming yellow.<sup>1</sup> The colour remains on warming,<sup>2</sup> and cannot be extracted by ether.<sup>3</sup> Moreover, when molybdic anhydride,  $\text{MoO}_3$ , is dissolved in hydrogen peroxide, a yellow insoluble compound is deposited from the stable, dark yellow solution.<sup>4</sup>

Pécharde<sup>5</sup> regarded the compound which he obtained both by double decomposition of the barium salt with sulphuric acid, and by dissolving molybdenum or certain of its oxides in hydrogen peroxide, as  $\text{HMoO}_4 \cdot 2\text{H}_2\text{O}$ . The compound so obtained, although reasonably stable, is an active oxidising agent; hydrogen chloride is, for instance, oxidised to chlorine, but other strong acids are not attacked. Pécharde describes several permolybdates, and assigns to them the formulæ  $\text{KMoO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NH}_4\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , etc., thus indicating their analogy to the persulphates of the type  $\text{R}'_2\text{S}_2\text{O}_8$ ; <sup>6</sup> it is not yet certain, however, that compounds of this type ( $\text{R}'\text{MoO}_4$ ) actually exist.<sup>7</sup> In fact, although Cammerer's<sup>8</sup> formula,  $2\text{MoO}_3 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ , is comparable with that of Pécharde, Pissarjewsky has prepared, by Pécharde's method, a compound to which he assigns the formula  $\text{H}_2\text{MoO}_5 \cdot 2\text{H}_2\text{O}$ . By interaction of molybdenum trioxide with 25 per cent. hydrogen peroxide, another hydrate of the acid  $\text{H}_2\text{MoO}_5$ —probably  $2\text{H}_2\text{MoO}_5 \cdot 3\text{H}_2\text{O}$ —has<sup>9</sup> been prepared.

From a study of the heat evolution on dissolving molybdic anhydride in varying quantities of hydrogen peroxide,<sup>10</sup> and of the distribution of hydrogen peroxide between ether and aqueous molybdic acid,<sup>11</sup> it is indicated that at least two permolybdic acids exist in acid solutions: (a)  $\text{H}_2\text{MoO}_5$  or  $\text{MoO}_3 \cdot \text{H}_2\text{O}_2$ , and (b)  $\text{H}_2\text{MoO}_6$ . The constitution of these two compounds is not established. The molybdenum appears to be in the hexavalent state, and the following alternative structural formulæ have been suggested:<sup>12</sup>



<sup>1</sup> Werthier, *J. prakt. Chem.*, 1861, 83, 195; 84, 198. Cf. Schönn, *Zeitsch. anal. Chem.*, 1870, 9, 41, 311.

<sup>2</sup> Denigès, *Compt. rend.*, 1890, 110, 1007.

<sup>3</sup> Bürwald, *Chem. Zentr.*, 1885, p. 424.

<sup>4</sup> Fairley, *Trans. Chem. Soc.*, 1877, 31, 141.

<sup>5</sup> Pécharde, *Compt. rend.*, 1891, 112, 628; 1892, 114, 1481; 1892, 115, 227.

<sup>6</sup> See Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1898, 18, 59; Moeller, *Zeitsch. physikal. Chem.*, 1893, 12, 555.

<sup>7</sup> Muthmann and Nagel, *Zeitsch. anorg. Chem.*, 1898, 17, 73; Pissarjewsky, *ibid.*, 1900, 24, 108.

<sup>8</sup> Cammerer, *Chem. Zeit.*, 1891, 15, 957.

<sup>9</sup> Muthmann and Nagel, *Ber.*, 1898, 12, 555.

<sup>10</sup> Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 210; *Zeitsch. physikal. Chem.*, 1902, 40, 368.

<sup>11</sup> Brode, *Zeitsch. physikal. Chem.*, 1901, 37, 299.

<sup>12</sup> Pissarjewsky, *Zeitsch. anorg. Chem.*, 1900, 24, 108; Brode, *loc. cit.* See Price, *Peroxyacids and their Salts* (Longmans, Green & Co.), 1912, p. 103; Koppel, *Abegg's Handbuch der anorganischen Chemie* (Leipzig, 1921), vol. iv., 1, 2nd half, p. 656.

As to the permolybdates, potassium, rubidium, caesium, ammonium, and barium salts have <sup>1</sup> been prepared. The formulæ ascribed are somewhat complex; for example, for the orange-red ammonium salt (obtained by the action of hydrogen peroxide on a solution of ordinary ammonium molybdate),  $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_4 \cdot 12\text{H}_2\text{O}$ , and for the lemon-yellow ammonium salt (obtained by concentration of the mother-liquor of the orange-red salt),  $3(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot 2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$ . The aqueous solution of these salts contains hydrogen peroxide, and is readily decomposed by small quantities of alkali. Another salt,  $\text{K}_2\text{O}_2 \cdot \text{MoO}_3 \cdot \text{H}_2\text{O}_2$ , or  $\text{K}_2\text{MoO}_6 \cdot \text{H}_2\text{O}$ , has <sup>2</sup> been prepared as an unstable solid evolving oxygen on treatment with water, by interaction of cooled solutions of hydrogen peroxide, potassium hydroxide, and Péchard's potassium permolybdate, and precipitation at a low temperature with alcohol.

Fluoropermolybdates,<sup>3</sup> and oxalo- and other organo- salts of the peroxide,<sup>4</sup> have also been described.

### MOLYBDENUM AND SULPHUR.

**Molybdenum Sesquisulphide,  $\text{Mo}_2\text{S}_3$ .**—When the disulphide, compressed into small bars, is heated in an electric furnace, a metallic mass is produced which consists of the sesquisulphide,  $\text{Mo}_2\text{S}_3$ , contaminated with metallic molybdenum. On removal of the latter with aqua regia, there are obtained steel-grey needles, of density 5.9, which are readily reduced to the metal by heating in hydrogen, or converted to the disulphide by heating in sulphur-vapour.<sup>5</sup>

**Molybdenum Disulphide,  $\text{MoS}_2$ ,** occurs in nature as *molybdenite* (see p. 111),<sup>6</sup> but may also be obtained by the action of sulphur or hydrogen sulphide upon molybdic anhydride;<sup>7</sup> by fusion together of sodium molybdate, molybdic anhydride, and sulphur; or by heating the sesquisulphide out of contact with air. A crystalline disulphide is conveniently obtained <sup>5</sup> by heating together potassium carbonate, sulphur, and molybdenum dioxide or ammonium molybdate, and extracting the cooled mass with water; an amorphous form is obtained by heating together finely powdered ammonium molybdate and sulphur, and reheating the mass after the addition of a further quantity of sulphur.

Molybdenum disulphide is decomposed—yielding the sesquisulphide and molybdenum—only at the temperature of the electric furnace. It is attacked by chlorine, bromine, nitric acid, sulphuric acid, and, when strongly heated, by hydrogen or water-vapour, but not by alkalies.<sup>8</sup> The specific heat of the naturally occurring molybdenite is 0.1067 (Neumann), and of the artificial, 0.1233 (Regnault).

<sup>1</sup> Bärwald, *loc. cit.*; Muthmann and Nagel, *Zeitsch. anorg. Chem.*, 1898, 17, 73; Struve, *J. prakt. Chem.*, 1853, 58, 493.

<sup>2</sup> Melikoff and Pissarjewsky, *Ber.*, 1898, 31, 632, 2448; *Zeitsch. anorg. Chem.*, 1899, 19, 414. Cf. Muthmann and Nagel, *loc. cit.*

<sup>3</sup> Piccini, *Zeitsch. anorg. Chem.*, 1892, 1, 51; Kazanetsky, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 383.

<sup>4</sup> Mazzucchelli and others, *Atti R. Accad. Lincei*, 1907, [5], 16, i., 963; 1909, [5], 18, ii., 259; *Gazzetta*, 1910, 40, ii., 49, 241; 1914, 43, ii., 116, 426.

<sup>5</sup> Guichard, *Ann. Chim. Phys.*, 1901, [7], 23, 557.

<sup>6</sup> See also de Schulten, *Bull. Soc. franç. Min.*, 1889, 12, 545; Guichard, *loc. cit.*

<sup>7</sup> The reaction is not, however, complete. See Svanberg and Struve, *J. prakt. Chem.*, 1848, 44, 257.

<sup>8</sup> See von der Pfordten, *Ber.*, 1885, 17, 731; Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 385.

The electrical properties and thermionic emission of molybdenite have been investigated;<sup>1</sup> the mineral appears to exist in two states between atmospheric temperature and red heat, and at temperatures above 310° C. a characteristic emission of positive molybdenum ions occurs.

**Dimolybdenum Pentasulphide** is obtained<sup>2</sup> as a trihydrate,  $\text{Mo}_2\text{S}_5 \cdot 3\text{H}_2\text{O}$ , by reducing with zinc a solution of ammonium molybdate containing more than 20 per cent. of sulphuric acid. When the solution becomes dark red it is diluted, filtered, and saturated with hydrogen sulphide, and the resulting precipitate, after successively washing with hot water, alcohol, carbon disulphide, and ether, is dried at about 70° C. The trihydrate loses one-third of its water at 140° C., but decomposes on further heating. When carefully heated in carbon dioxide, the anhydrous pentasulphide,  $\text{Mo}_2\text{S}_5$ , is obtained as an almost black compound.

**Molybdenum Trisulphide,  $\text{MoS}_3$ ,** is obtained by saturating an alkali molybdate with hydrogen sulphide (or by adding thereto ammonium sulphide), and decomposing the thiomolybdate so formed by warming with dilute hydrochloric or sulphuric acid. There is thus obtained a reddish-brown gelatinous precipitate, which on drying becomes dark brown. It is slightly soluble in water and in aqueous potassium hydroxide, but easily soluble in a solution of potassium sulphide.<sup>3</sup> On heating it yields the disulphide  $\text{MoS}_2$ ; at a high temperature in hydrogen it is reduced to the metal.<sup>4</sup> Molybdenum trisulphide has been prepared<sup>5</sup> in the colloidal condition.

**Molybdenum Tetrasulphide,  $\text{MoS}_4$ ,** is formed by decomposition of a perthiomolybdate with a dilute acid.<sup>6</sup>

A solution is made of potassium dimolybdate (30 grams  $\text{MoO}_3$  fused with 14.4 grams  $\text{K}_2\text{CO}_3$ ) in 120 c.c. of hot water; this solution, after filtration, is diluted with 350 c.c. of water, and saturated at 15° C. with hydrogen sulphide. The liquid is then evaporated on the water-bath up to crystallising point. There is deposited on cooling not only potassium perthiomolybdate,  $\text{KHMOS}_5$ , but also the di- and tri-sulphides of molybdenum, and gelatinous thiomolybdates. The mass is thoroughly extracted with ice-cold water, then dissolved in water at 30° to 40° C., and precipitated with hydrochloric acid. This precipitate, well washed with water, alcohol, and carbon disulphide, and dried in an atmosphere of hydrogen sulphide at 140° C., is the anhydrous tetrasulphide.

This brownish powder, which is somewhat unstable in the air, and which is soluble in potassium sulphide solution, is also obtained in small quantity by the interaction of molybdenum trisulphide and potassium sulphide.

<sup>1</sup> Waterman, *Phil. Mag.*, 1917, [6], 33, 225; *Phys. Review*, 1923, 21, 540; Collet, *Compt. rend.*, 1914, 158, 1994. The behaviour of molybdenite as an electrode has been studied by Smith (*Ber.*, 1890, 23, 2276) and Bernfeld (*Zeitsch. physikal. Chem.*, 1898, 25, 46). On the crystal structure of molybdenite, see Dickinson and Pauling, *J. Amer. Chem. Soc.*, 1923, 45, 1466. On the photo-electrical sensitivity of molybdenum disulphide, see Soblentz, *U.S. Bureau of Standards, Science Papers*, 1922, 18, 585.

<sup>2</sup> Mawrow and Nikolow, *Zeitsch. anorg. Chem.*, 1916, 95, 188.

<sup>3</sup> Berzelius, *Pogg. Annalen*, 1826, 7, 429.

<sup>4</sup> von der Pfordten, *Ber.*, 1885, 17, 731.

<sup>5</sup> Winninger, *Bull. Acad. roy. Belg.*, 1888, [3], 15, 390.

<sup>6</sup> Krüss, *Annalen*, 1884, 225, 40; Berzelius, *Pogg. Annalen*, 1826, 7, 261.

Of the *thio-acids* corresponding to the sulphides of molybdenum, two have been prepared, namely, hexathiomolybdic acid,  $\text{HMoS}_6$ , and perthiomolybdic acid,  $\text{H}_2\text{MoS}_5$ . The former has been obtained <sup>1</sup> by decomposition of the ammonium salt with hydrochloric acid; the latter is precipitated as a reddish-brown powder on the addition of dilute acetic acid to a solution of its potassium salt,  $\text{KHMoS}_5$ .<sup>2</sup>

**Thiomolybdates.**—A large number of compounds have been described. Besides the normal salts,  $\text{R}_2\text{MoS}_4$ , basic compounds of the type  $\text{R}_6\text{Mo}_2\text{S}_9$ , and acid salts of the type <sup>3</sup>  $\text{R}'\text{S}.3\text{MoS}_3$ , have been prepared. Oxythiomolybdates, compounds intermediate between the molybdates and thiomolybdates, are also known.

**Ammonium Thiomolybdates.**—By passing a current of hydrogen sulphide into an ammoniacal solution of (ordinary) ammonium molybdate, or by dissolving molybdenum trisulphide in ammonium sulphide solution, and concentrating by evaporating, blood-red crystals, appearing green by reflected light, of the normal salt  $(\text{NH}_4)_2\text{MoS}_4$  are obtained. They are not completely stable in air.<sup>4</sup> The compound  $\text{NH}_4\text{MoS}_6\cdot\text{H}_2\text{O}$  has also been described.<sup>1</sup>

By addition of a solution of ammonium hydrogen sulphide drop by drop to one of ammonium molybdate, the compound  $(\text{NH}_4)\text{HMoS}_3\text{O}_4$  is precipitated as a reddish-yellow substance.<sup>5</sup> Another mixed salt has the formula  $(\text{NH}_4\text{O})_2\text{MoS}_2$ .<sup>6</sup>

**Ammonium Molybdosulphites**, of the formulæ  $4(\text{NH}_4)_2\text{O}.3\text{SO}_2$ ,  $10\text{MoO}_3.6\text{H}_2\text{O}$  and  $4(\text{NH}_4\text{K})\text{O}.3\text{SO}_2.10\text{MoO}_3.9\text{H}_2\text{O}$ , have been prepared;<sup>7</sup> there are also known<sup>8</sup> the *molybdosulphates*  $(\text{NH}_4)_2\text{O}.2\text{MoO}_3.3\text{SO}_3.10\text{H}_2\text{O}$ ;  $(\text{NH}_4)_2\text{O}.2\text{MoO}_3.\text{SO}_3.9\text{H}_2\text{O}$  and  $4\text{H}_2\text{O}$ ;  $5\text{NH}_3.\text{MoO}_2.\text{SO}_3.7\text{MoO}_3.8\text{H}_2\text{O}$  and  $3\text{NH}_3.\text{MoO}_2.\text{SO}_3.7\text{MoO}_3.10\text{H}_2\text{O}$ .

**Potassium Thiomolybdates.**<sup>9</sup>—A normal salt, a thiodimolybdate, a basic salt, and molybdates in which the oxygen is only partially replaced by sulphur, have been prepared.

**Potassium Thiomolybdate**,  $\text{K}_2\text{MoS}_4$ , is prepared, according to Berzelius (*loc. cit.*), by gradually heating to bright redness a mixture of molybdenum disulphide, potassium carbonate, sulphur, and a little powdered charcoal. The water solution of the cold black melt is dark red in colour, and on gentle evaporation yields crystals which may be further purified by precipitation of their aqueous solution with alcohol. The substance is not entirely stable.<sup>10</sup>

**Potassium Thiodimolybdate**,  $\text{K}_2\text{Mo}_2\text{S}_7$ , is obtained as a dark grey substance on addition of a deficiency of mineral acid (preferably acetic acid) to an aqueous solution of the normal thiomolybdate and evaporation of the brown liquid.

The compound  $\text{K}_6\text{Mo}_2\text{S}_9$  results from the passage of hydrogen sul-

<sup>1</sup> Hofmann, *Zeitsch. anorg. Chem.*, 1896, 12, 55.

<sup>2</sup> Krüss, *Annalen*, 1884, 225, 40.

<sup>3</sup>  $\text{R}' = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ . See Berzelius, *Pogg. Annalen*, 1826, 7, 262.

<sup>4</sup> Krüss, *Annalen*, 1884, 225, 29; Berzelius, *Traité de Chimie*, 1847, 3, 321; Braun, *Zeitsch. anal. Chem.*, 1867, 6, 89.

<sup>5</sup> Krüss, *loc. cit.*; Krüss and Solleder, *Ber.*, 1886, 19, 2729; Debray, *Compt. rend.*, 1858, 46, 1102; Bodenslab, *J. prakt. Chem.*, 1859, 78, 186.

<sup>7</sup> Péchard, *Compt. rend.*, 1893, 116, 1441.

<sup>8</sup> Péchard, *ibid.*, 1901, 132, 628; Weinland and Kühl, *Zeitsch. anorg. Chem.*, 1907, 54, 259.

<sup>9</sup> Berzelius, *Traité de Chimie*, 1835, 4, 140.

<sup>10</sup> Krüss and Solleder, *loc. cit.*

phide through a 5 per cent. solution of normal potassium molybdate containing a sufficient excess of potash.<sup>1</sup> The aqueous solution is orange-yellow in colour.

**Potassium Dithiodioxymolybdate**,  $K_2MoO_2S_2$ , separates as yellow needles from the oily liquid obtained when finely powdered dry potassium trimolybdate is added to a somewhat warm solution of potassium hydrogen sulphide, and alcohol added.<sup>2</sup> It is a hygroscopic substance, soluble in water, and readily decomposed by mineral acids. A compound  $K_3Mo_4S_9O_7$  is also said to be obtained from the oily liquid. A compound  $KHMo_2S_3O_7$  is also known,<sup>1</sup> as well as the salts  $KHMoS_5$ <sup>3</sup> and  $KMoS_6.H_2O$ .<sup>4</sup>

**Potassium Molybdosulphite**,  $4K_2O.3SO_2.10MoO_3.10H_2O$ , and *molybdosulphates*,  $K_2O.2MoO_3.3SO_3.6H_2O$  and  $K_2O.2MoO_3.SO_3.6H_2O$  or  $2H_2O$ ,<sup>5</sup> are mentioned in the literature, together with the *compounds*  $2K_2S.2MoS_3.As_2S_5.8H_2O$ ;  $K_4Mo_2As_2O_3S_{10}.6H_2O$ ; <sup>6</sup>  $KMoAsO_2S_4.2\frac{1}{2}H_2O$ ,<sup>7</sup> and  $MoS_2(CN)_2.4KCN$ .

**Sodium Thiomolybdates**.—Two are known: the normal salt,  $Na_2MoS_4$ , prepared as dark reddish crystals by the action of hydrogen sulphide upon a solution of sodium molybdate, and the acid salt,  $Na_2Mo_2S_7$ , obtained as a dark grey mass by treatment of the normal salt with a deficiency of acid.<sup>8</sup> Oxythiomolybdates are obtained<sup>9</sup> by the action of sodium hydrosulphide upon sodium tri- and para-molybdates.

**Sodium Molybdosulphites**,  $4Na_2O.10MoO_3.3SO_2.12H_2O$  and  $16H_2O$ , have been described,<sup>5</sup> and the *compounds*  $2Na_2S.As_2S_5.2MoS_3.14H_2O$  and  $NaAsS_3.MoS_3.6H_2O$ .<sup>7</sup>

No acid corresponding to the molybdosulphites has been isolated.

**Molybdenum Sulphates**.—Reduction of a solution of molybdic acid in sulphuric acid by means of hydrogen sulphide is stated<sup>10</sup> to yield the compound  $MoO_3.MoO_2.2SO_3$  as a black substance, soluble in water to an unstable brown solution; <sup>11</sup> reduction with alcohol is said<sup>12</sup> to yield soluble blue crystals of the sulphate  $7MoO_3.2MoO_2.7SO_3.aq$ .

The sulphate  $Mo_2(SO_4)_3.2H_2O$  has been described,<sup>13</sup> but its existence has not been confirmed.<sup>14</sup>

A compound of molybdenum trioxide with sulphur trioxide,  $MoO_3.SO_3$ , has, however, been obtained<sup>14</sup> as deliquescent, soluble crystals<sup>15</sup> when molybdenum trioxide is dissolved in warm concentrated sulphuric acid.

An *oxysulphate*,  $Mo_2O(SO_4)_2.xH_2O$  ( $x=5$  or  $6$ ), is formed as a green

<sup>1</sup> Krüss, *Annalen*, 1884, 225, 33.

<sup>2</sup> Rosenheim and Itzig, *Ber.*, 1900, 33, 707.

<sup>3</sup> Krüss and Solereider, *loc. cit.*; Berzelius, *loc. cit.*; Krüss, *loc. cit.*

<sup>4</sup> Hofmann, *Zeitsch. anorg. Chem.*, 1896, 12, 55.

<sup>5</sup> Péchard, *Compt. rend.*, 1893, 116, 1441.

<sup>6</sup> Péchard, *ibid.*, 1901, 132, 628; Weinland and Kühn, *Zeitsch. anorg. Chem.*, 1907, 54, 259.

<sup>7</sup> Weinland and Sommer, *Zeitsch. anorg. Chem.*, 1897, 15, 42.

<sup>8</sup> Berzelius, *Traité de Chimie*, 1835, 4, 140.

<sup>9</sup> Krüss, *Annalen*, 1884, 225, 6.

<sup>10</sup> Bailhache, *Compt. rend.*, 1901, 132, 475.

<sup>11</sup> On the action of sulphur dioxide on tri- and hexa-valent molybdenum in sulphuric acid solution, see Wardlaw and Sylvester, *Trans. Chem. Soc.*, 1923, 123, 969.

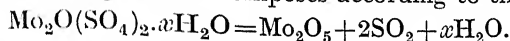
<sup>12</sup> Péchard, *Compt. rend.*, 1901, 132, 628.

<sup>13</sup> Anderson, *Berzelius' Jahresber.*, 1847, 22, 161.

<sup>14</sup> Schultze and Sallack, *Ber.*, 1871, 4, 14.

<sup>15</sup> Muthmann, *Annalen*, 1887, 238, 126; Rosenheim, *Zeitsch. anorg. Chem.*, 1894, 7, 176; 1897, 15, 180.

hygroscopic precipitate <sup>1</sup> when an electrolytically reduced solution of molybdenum trioxide in sulphuric acid is poured into air-free acetone. The salt possesses strong reducing properties, liberating copper and silver from their salts and reducing ferric and mercuric compounds. The sulphate radical is precipitated by barium chloride only on warming. On heating, the oxysulphate decomposes according to the equation :



The compound  $\text{Mo}_3\text{Br}_4\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , a yellow powder insoluble in water, results <sup>2</sup> from the interaction of molybdenum hydroxybromide,  $\text{Mo}_3\text{Br}_4(\text{OH})_2$  (p. 127), and sulphuric acid.

#### MOLYBDENUM AND SELENIUM.

**Molybdenum Selenide.**—On addition of mineral acids to solutions of molybdates through which hydrogen selenide has been passed, a brown precipitate of indefinite composition, but containing molybdenum selenide, is obtained.<sup>3</sup>

The acid  $5\text{MoO}_3 \cdot \text{SeO}_2 \cdot \text{aq.}$  has been obtained in aqueous solution.<sup>4</sup>

**Complex Molybdoselenites**, obtained by acidifying solutions containing alkali molybdate and selenite, have been described.<sup>5</sup> The composition of the products depends upon the ratio of molybdate to selenious acid present in the solution; when the selenium dioxide is in excess, the ratio  $\text{SeO}_2 : \text{MoO}_3$  is very nearly 1 : 1, and the following salts have been prepared :—

$2(\text{NH}_4)_2\text{O} \cdot 5\text{SeO}_2 \cdot 5\text{MoO}_3 \cdot 8\text{H}_2\text{O}$ , white microscopic prisms ;

$2\text{K}_2\text{O} \cdot 4\text{SeO}_2 \cdot 4\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ , microscopic prisms ;

$\text{BaO} \cdot 2\text{SeO}_2 \cdot 2\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ , white crystals.

When less than 1 molecule of selenium dioxide is present to 1 molecule of molybdate, salts containing  $2\text{SeO}_2 : 5\text{MoO}_3$  and  $2\text{SeO}_2 : 8\text{MoO}_3$ , are obtained. Yellow uncrystallisable compounds containing  $2\text{SeO}_2 : 12\text{MoO}_3$  have also been described.<sup>6</sup>

Molybdenum telluride has not been obtained.

#### MOLYBDENUM AND CHROMIUM.

Molybdenum and chromium *alloy* in the electric furnace ; <sup>7</sup> reduction of the mixed oxides by aluminium also produces alloys.<sup>8</sup>

**Chromates of Molybdenum**,<sup>9</sup> and a *bromochromate*,  $\text{Mo}_3\text{Br}_4 \cdot \text{CrO}_4 \cdot 2\text{H}_2\text{O}$ , have been described.

A double sulphide of chromium and molybdenum,  $\text{Cr}_2\text{S}_6(\text{MoS}_2)_3$ , also finds mention in the literature.

**Chromimolybdates and Chromimolybdic Acid** have been described (see p. 142).

<sup>1</sup> Wardlaw, Nicholls, and Sylvester, *Trans. Chem. Soc.*, 1924, 125, 1910.

<sup>2</sup> Blomstrand, *J. prakt. Chem.*, 1859, 77, 89; 1861, 82, 437.

<sup>3</sup> Tuttle, *Annalen*, 1857, 101, 285; Uelsmann, *ibid.*, 1860, 116, 125.

<sup>4</sup> Péchard, *Compt. rend.*, 1893, 117, 104.

<sup>5</sup> Prandtl and von Blochin, *Zeitsch. anorg. Chem.*, 1915, 93, 45; Rosenheim and Krause, *ibid.*, 1921, 118, 177.

<sup>6</sup> Prandtl, von Blochin, and Obpacher, *ibid.*, 1915, 93, 45.

<sup>7</sup> Sargent, *J. Amer. Chem. Soc.*, 1900, 22, 783; Haynes, *J. Ind. Eng. Chem.*, 1913, 5, 189.

<sup>8</sup> Stavenhagen and Schuchard, *Ber.*, 1902, 35, 909.

<sup>9</sup> Berzelius, *Pogg. Annalen*, 1825, 6, 384; Calcagni, *Gazzetta*, 1925, 55, 396.



## MOLYBDENUM AND NITROGEN.

Molybdenum chloride and dry ammonia react at a fairly low temperature with formation of ammonium chloride and a grey substance which, after extraction with water to remove ammonium and molybdenum chlorides, and warming in air, is spontaneously inflammable.<sup>1</sup> The composition, however, of such a substance, or of that obtained by sublimation of molybdenum chloride with ammonium chloride, is apparently not definitely known.<sup>2</sup>

It has been found<sup>3</sup> that when molybdenum oxide, hydroxide, or a mixture of either of these compounds with the metal, is heated at 500° to 600° C. with equal parts of nitrogen and hydrogen under a pressure of 60 atmospheres, there is formed a *nitride* of molybdenum. The same compound may be obtained under atmospheric pressure by reducing pure precipitated molybdic acid by means of hydrogen at 700° C., and then passing nitrogen over the product at the same temperature.<sup>4</sup> The commercial importance of this substance lies in the fact that on heating in a vacuum it yields pure metallic molybdenum, with simultaneous liberation of ammonia.

The existence of a compound,  $\text{MoO}_2(\text{NH}_2)_2$ , **molybdamide**, obtained by interaction of ammonia with the oxychloride  $\text{MoO}_2\text{Cl}_2$ , and yielding ammonia when treated with water, has been noted.<sup>5</sup>

Nitrates of molybdenum are not known. By digesting dilute nitric acid with excess of molybdenum, or with the hydrate of molybdenum dioxide or sesquioxide, a dark brown solution is obtained, which on further evaporation yields oxides of nitrogen and molybdic acid.

## MOLYBDENUM AND PHOSPHORUS.

**Molybdenum Phosphide, MoP**, is formed<sup>6</sup> when molybdenum trioxide is fused with phosphoric acid and a little chalk, and the grey crystalline metallic mass is extracted first with hydrochloric acid and then with caustic soda. It has density 6.17, and is readily oxidised on heating in air, treating with nitric acid, or fusing with potassium nitrate.

**Molybdic Metaphosphate** has been prepared<sup>7</sup> by the reduction, at red heat, of a solution of molybdenum trioxide in metaphosphoric acid, either by hydrogen or by molybdenum disulphide in a current of carbon dioxide. It is also obtained by heating molybdenum disulphide or the dioxide<sup>8</sup> with orthophosphoric acid in a current of carbon dioxide. It is a yellow crystalline powder, of composition  $\text{Mo}_2\text{O}_5 \cdot 3\text{P}_2\text{O}_5$ , or  $\text{Mo}(\text{PO}_3)_3$ , stable in dry air, and of density at 0° C. = 3.28. On heating, it is only oxidised superficially; heated with water in a sealed tube, it is decomposed at 250° to 300° C., forming orthophosphoric acid. Hot concentrated mineral acids have no action upon it, but it dissolves slowly in warm aqua regia, and it is readily attacked by hot caustic alkali. It forms double phosphates when fused with alkali phosphates.

<sup>1</sup> Uhrlaub, *Pogg. Annalen*, 1857, **101**, 605.

<sup>2</sup> Tuttle, *Annalen*, 1857, **101**, 285; Debray, *ibid.*, 1858, **108**, 258.

<sup>3</sup> Badische Anilin- und Soda-Fabrik, *German Patent*, 246554 (1912).

<sup>4</sup> Badische Anilin- und Soda-Fabrik, *German Patent*, 62524 (1914).

<sup>5</sup> Smith and Fleck, *Zeitsch. anorg. Chem.*, 1894, **7**, 351.

<sup>6</sup> Wöhler and Rautenberg, *Annalen*, 1859, **109**, 374.

<sup>7</sup> Colani, *Compt. rend.*, 1914, **158**, 499.

<sup>8</sup> Colani, *ibid.*, 1917, **165**, 185.

Other simple phosphates of trivalent molybdenum have not been prepared, but the complex salt, sodium molybdenipyrophosphate,  $\text{Na}(\text{MoP}_2\text{O}_7)_{12}\text{H}_2\text{O}$ , has been obtained <sup>1</sup> as a brown crystalline precipitate by adding tripotassium molybdenum hexachloride,  $\text{K}_3\text{MoCl}_6$ , to a solution of sodium pyrophosphate at 80° to 90° C.

### Heteropoly-compounds of Molybdenum and Phosphorus.

Heteropoly-compounds include those acids and salts which contain acid anhydrides of one or more elements combined with a hydrate or salt of the acid of another element.<sup>2</sup> Compounds which contain the acid anhydride and the acid hydrate or salt of the *same* element—for example, polychromates, polytungstates, etc. are distinguished as isopoly-compounds.

Perhaps the most characteristic group of heteropoly-compounds is that of the phosphomolybdic acids which have hitherto been considered as complex acids. Much early work <sup>3</sup> was directed towards the action of phosphoric acid on molybdic acid and the alkali molybdates with the object of explaining the nature of the products obtained. It was shown that when molybdic anhydride dissolved in orthophosphoric acid a yellow solution was obtained, which on evaporation gave a viscous uncrystallisable liquid. On adding ammonia to the yellow solution a yellow precipitate was obtained in the presence of acid. The precipitation was impeded by the presence of certain organic salts, e.g. ammonium oxalate or citrate, and the meta- and pyro-phosphoric acids only gave the reaction after being converted to the ortho-acid.<sup>4</sup> The yellow precipitate was shown to be the ammonium salt of a definite phosphomolybdic acid, which was isolated from it by Debray <sup>5</sup> by gently heating with excess of aqua regia, when the ammonia was expelled and a yellow solution remained which by spontaneous evaporation gave crystals of the acid, to which he assigned the formula  $\text{P}_2\text{O}_5 \cdot 20\text{MoO}_3 \cdot 25\text{H}_2\text{O}$ . It forms yellow salts, those of potassium, ammonium, rubidium, cesium, and thallium being insoluble in water.

The yellow phosphomolybdates are decomposed by excess of alkali, giving neutral molybdates and other white phosphomolybdates, soluble in alkaline solution and richer in phosphoric acid. These white salts are reconverted to yellow phosphomolybdates with liberation of phosphoric acid by the action of acids.

The composition of phosphomolybdic acid given by Debray was contested by Rammelsberg,<sup>6</sup> who found the ratio  $\text{P}_2\text{O}_5 : \text{MoO}_3$  to be 1 : 22, while other workers found 1 : 24.<sup>7</sup> Numerous other combinations in which the proportion of the two oxides varied considerably have been described.<sup>8</sup>

The study of these complex compounds was simplified by the

<sup>1</sup> Rosenheim and Triantaphyllides, *Ber.*, 1915, 48, 582.

<sup>2</sup> Rosenheim and Kohn, *Zeitsch. anorg. Chem.*, 1911, 69, 247.

<sup>3</sup> Berzelius, *Traité de Chimie*, 1847, 4, 387; Svanberg and Struve, *J. prakt. Chem.*, 1848, 44, 257; 1851, 54, 288; Sonnenschein, *Ann. Chem. Phys.*, 1853, [3], 37, 58; Eggertz, *Bull. Soc. chim.*, 1860, 2, 328; Lipowitz, *ibid.*, 1860, 2, 117; Koenig, *ibid.*, 1872, 17, 208.

<sup>4</sup> Rose, *Pogg. Annalen*, 1849, 76, 26.

<sup>5</sup> Debray, *Compt. rend.*, 1868, 66, 702, 732.

<sup>6</sup> Rammelsberg, *Ber.*, 1877, 10, 1776.

<sup>7</sup> Finkener, *Ber.*, 1878, 11, 1638; Gibbs, *Amer. Chem. J.*, 1881, 3, 317; von der Pfordten, *Ber.*, 1882, 15, 1929; Hundeshagen, *Zeitsch. anal. Chem.*, 1889, 28, 141; Pemberton, *Ber.*, 1882, 15, 2635.

<sup>8</sup> Gibbs, *loc. cit.*; Richter, *Zeitsch. anal. Chem.*, 1871, 10, 471; Stünkel, Wetzke, and Wagner, *ibid.*, 1882, 21, 353; Hehner, *ibid.*, 1882, 21, 508.

application of the electrical conductivity as an indicator in the neutralisation of acids,<sup>1</sup> and it was found that the phosphomolybdates and other heteropoly-compounds could be satisfactorily formulated by the application of a modification of Werner's co-ordination theory suggested by Miolati<sup>2</sup> and extended by Rosenheim.<sup>3</sup> According to this theory, the complex phosphomolybdic compounds may be divided into two groups, the members of the first group possessing a heptavalent complex anion with phosphorus as the central atom, surrounded by six divalent atoms or groups of atoms. The anion is derived from  $[\text{PO}_6]'''$ , the oxygen atoms being replaced, wholly or in part, by the dimolybdate ion  $(\text{Mo}_2\text{O}_7)''$ . These complex anions are of a deep yellow colour, which is imparted to their salts in the absence of coloured cations. The members of the second group contain colourless anions derived from  $[\text{PO}_4]'''$ , the oxygen being replaced by the ion  $(\text{MoO}_4)''$ . Compounds are said to be *saturated* when all the oxygen atoms of the parent anion are replaced by metallic acid anions, unsaturated compounds containing some replaceable oxygen.<sup>4</sup>

**12-Molybdophosphoric Acid**,  $\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6] \cdot x\text{H}_2\text{O}$ , which is identical with the phosphomolybdic acid described above, may be obtained by heating the ammonium salt with aqua regia and recrystallising from water containing a little nitric acid; by dissolving the yellow hydrate,  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ , in a hot solution of phosphoric acid and allowing to crystallise; or by adding an excess of hydrochloric acid to a solution of an alkali molybdate and phosphoric acid and then extracting the molybdophosphoric acid with ether.<sup>5</sup>

It is readily soluble in water, and on evaporation the solution deposits deep yellow octahedral crystals of the *28-hydrate*  $\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6] \cdot 28\text{H}_2\text{O}$ . On heating this hydrate it begins to melt at about  $78^\circ \text{C}$ ., and a clear liquid is obtained at  $98^\circ \text{C}$ ., from which the *12-hydrate*  $\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6] \cdot 12\text{H}_2\text{O}$  may be separated in the form of minute crystals by carefully cooling to about  $90^\circ \text{C}$ . If the acid is crystallised from concentrated nitric acid solution, small rhombic crystals of a *22-hydrate*,  $\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6] \cdot 22\text{H}_2\text{O}$ , are obtained. Many other hydrates are described by earlier investigators, but there is little doubt that such were either identical with those described above or were not pure compounds.<sup>6</sup>

Salts of this acid have been prepared by treating a solution of an alkali molybdate with a small quantity of phosphoric acid; by adding a mineral acid, preferably concentrated nitric acid, to a solution containing a phosphate and a large excess of molybdate; or by boiling an aqueous solution of an alkali phosphate saturated with molybdic anhydride. The ammonium and potassium salts separate out as deep yellow micro-crystals, but the sodium salt is soluble, and is obtained by concentrating the solution when it forms yellow efflorescent rhombohedra. These salts have the approximate composition<sup>7</sup>

<sup>1</sup> Miolati and Mascetti, *Gazzetta*, 1901, **31**, i., 93.

<sup>2</sup> Miolati and Pizzighelli, *J. prakt. Chem.*, 1908, [2], **77**, 417.

<sup>3</sup> Rosenheim and Jüncke, *Zeitsch. anorg. Chem.*, 1917, **100**, 304.

<sup>4</sup> Rosenheim and Traube, *ibid.*, 1915, **91**, 75.

<sup>5</sup> Dreehsel, *Ber.*, 1887, **20**, 1452.

<sup>6</sup> See Debray, *Compt. rend.*, 1868, **66**, 702, 732; Gibbs, *loc. cit.*; Finkener, *Ber.*, 1878, **11**, 1638.

<sup>7</sup> On variations in the composition of the precipitated ammonium salt, see Posternak, *Compt. rend.*, 1920, **170**, 930.

$3R'_2O.P_2O_5.24MoO_3.xH_2O$ , where  $R' = NH_4$ , K, or Na. Corresponding salts of barium, cobalt, nickel, manganese, and iron have also been prepared<sup>1</sup> by boiling aqueous suspensions of the metallic phosphates with molybdic anhydride.

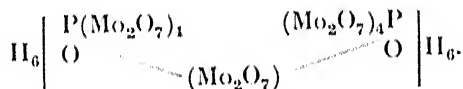
More exact information as to the nature of these compounds was obtained<sup>2</sup> by a study of the guanidinium salts. The *tribasic* salt, corresponding with those described above, is obtained by dissolving 12 molecules of molybdic anhydride in a boiling solution of guanidinium carbonate (containing 12 molecules), adding 1 molecule of phosphoric acid, and acidifying strongly with hydrochloric acid. The salt has the composition  $(CH_5N_3)_3H_7[P(Mo_2O_7)_6].10H_2O$ , and measurements of its electrical conductivity show it to be an acid salt. If a 10 per cent. solution of guanidinium carbonate is gradually mixed with a solution of 12-molybdophosphoric acid until the deep yellow precipitate first formed redissolves in the warm solution, greenish-yellow crystals of the *heptabasic* salt,  $(CH_5N_3)_7H_7[P(Mo_2O_7)_6].8H_2O$ , separate on cooling. Conductivity measurements prove this to be a normal salt.

The sodium salt described above has been shown<sup>3</sup> to be an acid salt of composition  $Na_3H_4[P(Mo_2O_7)_6].19H_2O$ . The heptabasic silver<sup>3</sup> and mercurous salts formed by precipitation from solutions of 12-molybdophosphoric acid by means of the metal nitrates are very probably the normal salts of the acid.

The existence of 11- and 10-molybdophosphoric acids and their salts, although many such have been described, is not established.

**9-Molybdophosphoric Acid, or Luteophosphomolybdic Acid,**  $H_{12}[P_2O_2(Mo_2O_7)_9].xH_2O$ , is formed by hydrolysis of the 12-molybdophosphoric acid, which takes place when an aqueous solution is allowed to stand for several days until it no longer gives precipitates with solutions of potassium or ammonium salts;<sup>4</sup> or by decomposing solutions of the trialkali phosphate with molybdic anhydride, adding sulphuric acid and extracting with ether.<sup>5</sup> It crystallises from solution in orange-coloured prisms, of composition  $H_{12}[P_2O_2(Mo_2O_7)_9].30H_2O$ , which in contact with the solution take up a further  $4H_2O$ , forming yellow crystals.

The acid is an unsaturated compound, the formula suggested for it being



The alkali salts are easily soluble in water and crystallise in the form of large orange-red prisms, and the salts of other bases can be obtained from them by double decomposition.

That these are acid salts is shown by conductivity measurements, the sodium salt,  $3Na_2O.P_2O_5.18MoO_3.31H_2O$ , being formulated by Rosenheim,  $Na_6H_6[P_2O_2(Mo_2O_7)_9].28H_2O$ . The neutral 12-basic guanidine salt,  $(CH_5N_3)_{12}H_{12}[P_2O_2(Mo_2O_7)_9].30H_2O$ , has been prepared,<sup>4</sup> and

<sup>1</sup> Arnfeld, *Dissertation*, Berlin, 1898.

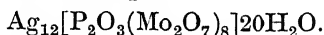
<sup>2</sup> Miolati and Pizzighelli, *loc. cit.*; Rosenheim and Pinsker, *Zeitsch. anorg. Chem.*, 1911, 70, 73.

<sup>3</sup> Gibbs, *Proc. Amer. Acad.*, 1882, 17, 75; Miolati and Pizzighelli, *loc. cit.*

<sup>4</sup> Rosenheim and Traube, *Zeitsch. anorg. Chem.*, 1915, 91, 75.

<sup>5</sup> Kehrman and Böhm, *ibid.*, 1894, 7, 406.

the corresponding rubidium salt,  $\text{Rb}_{12}[\text{P}_2\text{O}_3(\text{Mo}_2\text{O}_7)_9]10\text{H}_2\text{O}$ , has been described.<sup>1</sup> The precipitate obtained by addition of silver nitrate to a solution of the sodium acid salt, to which sodium hydroxide has been added to neutralise, has the composition



**17 : 2-Molybdophosphoric Acid**,  $\text{H}_{22}[\text{P}_4\text{O}_4(\text{Mo}_2\text{O}_7)_{17}]$ , is formed by further hydrolysis of 9-molybdophosphoric acid.<sup>2</sup> The potassium salt is obtained as a light yellow precipitate by treating a cold saturated solution of potassium hydrogen 9-molybdophosphate with potassium bicarbonate.<sup>3</sup> The ammonium and sodium salts are formed similarly, the composition of the former being  $(\text{NH}_4)_{16}\text{H}_6[\text{P}_4\text{O}_4(\text{Mo}_2\text{O}_7)_{17}]33\text{H}_2\text{O}$ . The normal salts of guanidinium and silver, respectively  $(\text{CH}_5\text{N}_3)_{22}\text{H}_{22}[\text{P}_4\text{O}_4(\text{Mo}_2\text{O}_7)_{17}]40\text{H}_2\text{O}$  and  $\text{Ag}_{22}[\text{P}_4\text{O}_4(\text{Mo}_2\text{O}_7)_{17}]40\text{H}_2\text{O}$ , have been prepared,<sup>2</sup> as well as the mixed salts  $\text{K}_{16}\text{Na}_6[\text{P}_4\text{O}_4(\text{Mo}_2\text{O}_7)_{17}]36\text{H}_2\text{O}$  and  $(\text{NH}_4)_{16}\text{Na}_6[\text{P}_4\text{O}_4(\text{Mo}_2\text{O}_7)_{17}]33\text{H}_2\text{O}$ ; the two latter are colourless salts formed by adding the chloride or bicarbonate of potassium or ammonium to a solution of sodium 12-molybdophosphate.

The white molybdophosphates formed when the yellow 12-molybdophosphates are treated with excess of alkali (see p. 163)<sup>4</sup> appear to approximate to the composition  $2\text{-}3\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 5\text{MoO}_3 \cdot x\text{H}_2\text{O}$ , where  $\text{R}=\text{NH}_4$ ,  $\text{K}$ ,  $\text{Na}$ ,  $\text{Li}$ , and  $\text{R}_2=\text{Mn}$ ,  $\text{Ni}$ ,  $\text{Co}$ , and there is evidence that they contain the complex anion  $[\text{P}_2\text{O}_4(\text{MoO}_4)_5]$ , which is 8-basic. The free acid, however, has not been isolated. Molybdopyrophosphates of composition  $2\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$  ( $\text{R}=\text{Na}$  or  $\text{Li}$ ) have been described.<sup>5</sup>

**Molybdohypophosphates.**—Sodium molybdohypophosphate,  $\text{Na}_2[\text{P}(\text{Mo}_2\text{O}_7)_3]8\text{H}_2\text{O}$ ,<sup>6</sup> is formed as a yellow crystalline precipitate when a solution of sodium hypophosphate,  $\text{Na}_2\text{PO}_3 \cdot 5\text{H}_2\text{O}$ , saturated at boiling temperature with molybdic anhydride, is cooled. It is sparingly soluble in water, the solution giving yellow amorphous precipitates with the chlorides of potassium, ammonium, and guanidinium.

**Molybdophosphites.**—If an acidified solution of ammonium molybdate is warmed with phosphorous acid, a light yellow crystalline precipitate of the ammonium salt,  $(\text{NH}_4)_2[\text{HP}(\text{Mo}_2\text{O}_7)_3]2\text{H}_2\text{O}$ , is formed, the reaction forming a delicate test for the presence of phosphorous acid.<sup>7</sup> The sodium salt,  $\text{Na}_2[\text{HP}(\text{Mo}_2\text{O}_7)_3]11\text{H}_2\text{O}$ , is slightly more soluble. It loses all its water at  $110^\circ \text{C}$ . The potassium, lithium, and guanidinium salts have been prepared.

Conductivity measurements show that these salts are derived from an acid which, like phosphorous acid, is dibasic, and must therefore contain the anion  $[\text{P}(\text{Mo}_2\text{O}_7)_3]''$ .

**Molybdohypophosphites.**—A solution containing sodium hypophosphite (1 molecule), sodium molybdate (4 molecules), and hydrochloric acid (7 molecules) gives, with ammonium chloride, white needles

<sup>1</sup> Ephraim and Herschfinkel, *Zeitsch. anorg. Chem.*, 1909, 64, 266.

<sup>2</sup> Rosenheim and Traube, *ibid.*, 1915, 91, 75. <sup>3</sup> Kehrman and Bühm, *ibid.*, 1894, 7, 406.

<sup>4</sup> See also Friedheim, *Zeitsch. anorg. Chem.*, 1893, 4, 272; Friedheim and Meschoirer, *ibid.*, 1894, 6, 83.

<sup>5</sup> Rosenheim and Schapiro, *ibid.*, 1923, 129, 196.

<sup>6</sup> Parravano and Marini, *Atti R. Accad. Lincei*, 1906, [5], 15, ii., 203; Rosenheim, Weinberg, and Pinsker, *Zeitsch. anorg. Chem.*, 1913, 84, 217; Müller, *ibid.*, 1916, 96, 29.

<sup>7</sup> Rosenheim, Weinberg, and Pinsker, *loc. cit.*; Rosenheim and Schapiro, *loc. cit.*

of the salt  $\text{NH}_4[\text{H}_2\text{P}(\text{Mo}_2\text{O}_7)_2]6\text{H}_2\text{O}$ .<sup>1</sup> The corresponding potassium and guanidinium salts have been prepared, but contained admixed trimolybdate.<sup>2</sup>

The halogen compounds,  $\text{MoCl}_5 \cdot \text{POCl}_3$ ; <sup>3</sup>  $\text{MoCl}_5 \cdot \text{PCl}_5$ ; <sup>4</sup>  $\text{MoCl}_4 \cdot \text{PCl}_5$  and  $\text{MoCl}_4 \cdot 2\text{PCl}_5$ ; <sup>5</sup> and  $\text{Mo}_3\text{Br}_4(\text{PO}_4\text{H}_2)_2$ ,<sup>6</sup> have been described.

### MOLYBDENUM AND ARSENIC.

Molybdenum arsenide has not been prepared. Molybdous arsenate is formed as a grey precipitate when molybdous chloride is treated with sodium arsenate; the precipitate first redissolves but afterwards becomes permanent. Molybdic arsenate, obtained in a similar manner from molybdic chloride, has been described by Berzelius, who also considered that an acid salt was produced on dissolving molybdic hydrate in excess of arsenic acid, since the solution turned blue on standing.<sup>7</sup>

Molybdic acid forms with arsenic acid a series of heteropoly-acids analogous to the molybdophosphoric acids described above. When a mixture of molybdic acid, arsenic acid, and an ammonium salt is boiled for some time, a yellow crystalline precipitate is obtained of an ammonium molybdo-arsenate. To this compound Debray<sup>8</sup> gave the formula  $3(\text{NH}_4)_2\text{O} \cdot \text{As}_2\text{O}_5 \cdot 20\text{MoO}_3$ , and considered that on boiling with aqua regia and evaporating the solution, the residue contained two acids—one yellow, in which the ratio of  $\text{As}_2\text{O}_5$  to  $\text{MoO}_3$  was 1 : 20, and the other white, with  $\text{As}_2\text{O}_5$  :  $\text{MoO}_3$  as 1 : 16. This was contested by Seyberth,<sup>9</sup> who considered that both the precipitate and the acid obtained from it contained  $\text{As}_2\text{O}_5$  :  $\text{MoO}_3$  : 1 : 7. Various other acids and salts have been described, in which the ratio of  $\text{As}_2\text{O}_5$  to  $\text{MoO}_3$  differs considerably, those compounds rich in molybdic acid generally being yellow in colour, while those containing less molybdic acid are white.<sup>10</sup> A satisfactory formulation of these compounds, showing their analogy to the molybdophosphates, is largely due to Rosenheim and his co-workers.

**12-Molybdo-arsenates.**—The free acid corresponding to the ordinary phosphomolybdic acid (see p. 164) has not been prepared, but the two acid salts,  $\text{R}_3\text{H}_4\text{As}(\text{Mo}_2\text{O}_7)_6 \cdot 4\text{H}_2\text{O}$ , where  $\text{R} = \text{NH}_4$  or  $\text{K}$  have been obtained in the form of deep yellow crystalline precipitate by adding arsenic acid in small quantities to solutions of the molybdates previously made acid with nitric acid and containing the alkali nitrates. The ammonium salt serves for the analytical detection of arsenic acid, and the precipitation is quantitative<sup>11</sup> providing the concentration of hydrogen ion present is greater than 0.030 per cent., as

<sup>1</sup> Rosenheim, Weinberg, and Pinsker, *loc. cit.*

<sup>2</sup> See also Mawrow, *Zeitsch. anorg. Chem.*, 1901, 28, 162; Mawrow and Nikolow, *ibid.* 1915, 92, 135.

<sup>3</sup> Blomstrand, *ibid.*, 1892, 1, 14.

<sup>4</sup> Smith and Sargent, *ibid.*, 1894, 6, 384.

<sup>5</sup> Cronander, *Bull. Soc. chim.*, 1873, [2], 19, 500.

<sup>6</sup> Smith and Maas, *Zeitsch. anorg. Chem.*, 1894, 5, 280.

<sup>7</sup> Berzelius, *Pogg. Annalen*, 1826, 6, 346; *Traité de Chimie*, 1847, 4, 498.

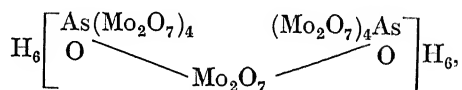
<sup>8</sup> Debray, *Compt. rend.*, 1874, 78, 1408. See also Struve, *J. prakt. Chem.*, 1853, 5, 493.

<sup>9</sup> Seyberth, *Ber.*, 1874, 7, 391.  
<sup>10</sup> See Debray, *loc. cit.*; Gibbs, *Amer. Chem. J.*, 1881 82, 3, 402; von der Pfordter, *Ber.*, 1882, 15, 1929; Pufahl, *ibid.*, 1884, 17, 217; Ditté, *Compt. rend.*, 1886, 102, 102.  
<sup>11</sup> Friedheim, *Zeitsch. anorg. Chem.*, 1892, 2, 314.

<sup>12</sup> Maderna, *Atti R. Accad. Lincei*, 1910, [5], 19, ii., 15.

that ammonium nitrate is present. In less acid or neutral solutions the precipitate is white, and contains less molybdenum than the yellow salt. The corresponding guanidinium salt has not been obtained, but when hydrochloric acid is added to a solution containing 12 molecules of guanidinium molybdate and 1 molecule of arsenic acid, deep yellow leaflets separate<sup>1</sup> of the 10-molybdo-arsenate,  $(\text{CH}_5\text{N}_3)_3\text{H}_7[\text{AsO}(\text{Mo}_2\text{O}_7)_5]5\text{H}_2\text{O}$ . By treating 1 molecule of this salt with 2 molecules of guanidinium carbonate, the heptabasic salt,  $(\text{CH}_5\text{N}_3)_7\cdot\text{H}_7[\text{AsO}(\text{Mo}_2\text{O}_7)_5]6\text{H}_2\text{O}$ , separates in the form of light yellow crystals which decompose when recrystallised. The conductivity corresponds with its formation as a normal salt. The free acid has not been prepared.

**9-Molybdo-arsenates.**—In this series the complex anion is more stable than in the two preceding series. The salts are derived from the acid,<sup>2</sup>



which is formed by agitation of a solution of sodium arsenate saturated with molybdic acid, with hydrochloric acid and ether. It is very soluble in water and yields two hydrates:  $\text{H}_{12}[\text{As}_2\text{O}_2(\text{Mo}_2\text{O}_7)_9]24\text{H}_2\text{O}$ , red crystals, stable at ordinary temperatures; and  $\text{H}_{12}[\text{As}_2\text{O}_2(\text{Mo}_2\text{O}_7)_9]34\text{H}_2\text{O}$ , yellow crystals, stable below 8° C. On treating the solution with alkali hydroxide or carbonate, the alkali salts are obtained. The sodium salt,  $\text{Na}_6\text{H}_6[\text{As}_2\text{O}_2(\text{Mo}_2\text{O}_7)_9]20\text{H}_2\text{O}$ , is yellow, and is an acid salt, indicating that the basicity of the acid is higher than 6.<sup>3</sup> On standing, the crystals of this salt crumble and change into a colourless 25-hydrate. The corresponding yellow potassium salt, containing  $11\text{H}_2\text{O}$ , changes similarly into a colourless 25-hydrate. Normal salts, of composition  $\text{R}'_{12}[\text{As}_2\text{O}_2(\text{Mo}_2\text{O}_7)_9]\cdot x\text{H}_2\text{O}$  ( $\text{R}' = \text{Cs}, \text{Ag}, \text{Tl}, \text{CH}_5\text{N}_3$ ), have been obtained by adding the metallic chloride to a solution of the yellow acid sodium salt, thus indicating that the basicity of the acid is 12.

Arsenic compounds corresponding to the 17-molybdo-2-phosphates (see p. 166) have not been prepared, but by mixing solutions of paramolybdates and alkali dihydrogen arsenates, white precipitates of composition  $5\text{R}'_2\text{O}\cdot\text{As}_2\text{O}_5\cdot 16\text{MoO}_3\cdot x\text{H}_2\text{O}$  ( $\text{R}' = \text{NH}_4\cdot\text{K}$ ) have been obtained,<sup>4</sup> which may be regarded as 8-molybdo-arsenates,  $\text{R}'_5[\text{As}(\text{OH})_2(\text{Mo}_2\text{O}_7)_4]\cdot(x-2)\text{H}_2\text{O}$ .

**3-Molybdo-arsenates.**—The complex anion of this series is the most stable of those derived from  $[\text{XO}_4]'''$  (see p. 164). The free acid,  $\text{H}_3[\text{AsO}(\text{MoO}_4)_3]$ , is tribasic, stronger than arsenic acid, and extremely stable, and is obtained on adding fuming nitric acid to a concentrated solution of arsenic acid saturated with molybdic acid. It readily dissolves in water, from which it may be crystallised in the form of white prisms.<sup>2</sup> The trisodium salt crystallises from water with  $11\cdot5\text{H}_2\text{O}$ , and the triguanidinium salt forms pale yellow anhydrous needles. Other salts have been described.<sup>5</sup>

<sup>1</sup> Rosenheim and Pinsker, *Zeitsch. anorg. Chem.*, 1911, 70, 73.

<sup>2</sup> Rosenheim and Traube, *ibid.*, 1915, 91, 75.

<sup>3</sup> Pufahl, *Ber.*, 1884, 17, 217; Rosenheim and Traube, *loc. cit.* See also Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49.

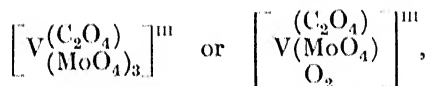
<sup>4</sup> Gibbs, *Amer. Chem. J.*, 1881–82, 3, 402; Friedheim, *Zeitsch. anorg. Chem.*, 1892, 2, 323.

<sup>5</sup> Pufahl, *loc. cit.*

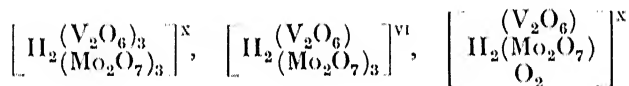
Salt of acids containing less molybdic acid—for example, 2- and 1-molybdo-arsenates of the types  $R_2H[AsO_2(MoO_4)_2].xH_2O$  and  $R'H_3[AsO_3(MoO_4)].xH_2O$ —have been described,<sup>1</sup> as also have sulphur-containing compounds of the types  $R_4[As_2S_5(MoS_4)_2].xH_2O$  and  $R'[AsS_2(MoS_4)].xH_2O$ .

Similar compounds with *antimony* have been mentioned,<sup>2</sup> but it has not yet been established that this element can function as the central atom of such complex anions or give rise to such series of heteropoly-compounds.

Vanadium, the first element in Subgroup 5A, and neighbour to chromium, is found in association with molybdenum in certain complex compounds. For example, when boiling solutions of molybdo-oxalates react with vanadium pentoxide, crystalline products are obtained which are thought to be substituted vanadates containing the complex anion



while other series of compounds are known, in which anions of the types



are supposed to function.<sup>3</sup> By the interaction of molybdic acid and alkali metavanadates in aqueous solution, a number of crystalline products have been obtained.<sup>4</sup> These appear to be complex molybdo-vanadates of two types which differ considerably in physical properties; those which are richer in vanadium yield large orange-red prisms, whilst those poorer in this element crystallise in yellow silky needles. Complex arsenomolybdo-vanadates have also been described.<sup>5</sup>

## MOLYBDENUM AND CARBON.

**Molybdenum Carbides.** The carbide,  $Mo_2C$ , may be obtained by heating molybdenum dioxide with carbon or with calcium carbide in an electric furnace.<sup>6</sup> The product shows a brilliant, white, crystalline fracture, cleaves readily, and has a density of 8.9. If a mixture of fused molybdenum, carbon, and excess of aluminium is heated in the electric furnace, the carbide,  $MoC$ , is obtained<sup>7</sup> as a grey crystalline powder, of density 8.40 at 20° C., and of hardness 7 to 8. It burns readily in fluorine, forming carbon tetrafluoride and molybdenum

<sup>1</sup> Friedheim, *loc. cit.*

<sup>2</sup> See Gibbs, *Proc. Amer. Acad.*, 1885, **21**, 89, 105; *Amer. Chem. J.*, 1885, **7**, 313, 392, 534; Hallopeau, *Compt. rend.*, 1896, **12**, 1065.

<sup>3</sup> Gibbs, *Amer. Chem. J.*, 1882, **83**, **4**, 377; 1883, **84**, **5**, 361, 374; Ditte, *Compt. rend.*, 1886, **102**, 757, 1019, 1105; Friedheim and Liebert, *Ber.*, 1891, **24**, 1173; Friedheim and Castendyck, *ibid.*, 1900, **33**, 1611; Prandtl, *Zeitsch. anorg. Chem.*, 1912, **79**, 97; Abegg, *Handbuch der anorganischen Chemie* (Leipzig, 1921), vol. iv., pt. 1, 2nd half, pp. 1039, 1052.

<sup>4</sup> Canneri, *Gazzetta*, 1923, **53**, 779; 1925, **55**, 390.

<sup>5</sup> Canneri, *ibid.*, 1923, **53**, 773.

<sup>6</sup> Moissan, *Compt. rend.*, 1895, **120**, 1320; 1897, **125**, 839.

<sup>7</sup> Moissan and Hoffmann, *ibid.*, 1904, **138**, 1558.



fluoride, and is attacked by chlorine, bromine, and iodine, but not by hydrogen, at higher temperatures. It is oxidised by heating in air or oxygen, or by the action of cold nitric acid, but is only slowly attacked by other mineral acids, and remains unaltered in solutions of alkali hydroxides.

Carbides of molybdenum have been prepared<sup>1</sup> by heating the finely powdered metal, or the trioxide, in a current of carbon monoxide or in a mixture of methane and hydrogen, and it was found from experiments at different temperatures that the limiting amount of carbon taken up corresponded with simple stoichiometric proportions. When molybdenum was heated with carbon monoxide, the product had the composition  $\text{Mo}_2\text{C}$  at  $600^\circ\text{C}$ . and  $1000^\circ\text{C}$ ., while at  $800^\circ\text{C}$ . the composition varied between  $\text{MoC}$  and  $\text{Mo}_2\text{C}_3$ .

**Molybdenum Carbonyl**,<sup>2</sup>  $\text{Mo}(\text{CO})_6$ , is formed when the finely divided metal is subjected to the action of carbon monoxide at a pressure of 200 to 250 atmospheres and at a temperature of  $200^\circ\text{C}$ . The metallic molybdenum must be in a sufficiently active form, and is best prepared by reducing an oxychloride by means of hydrogen at a low temperature; obtained in this way, it is just pyrophoric when gently warmed. The carbonyl forms highly refractive white crystals, of density 1.96 at  $15^\circ\text{C}$ . The crystals volatilise before melting, and can be sublimed in an atmosphere of hydrogen or carbon monoxide at a temperature of  $30^\circ$  or  $40^\circ\text{C}$ . The vapours decompose into molybdenum and carbon monoxide on heating above  $150^\circ\text{C}$ . Its chemical properties resemble those of other carbonyls. It is readily attacked by oxidising agents, especially bromine, which liberates carbon monoxide and retains molybdic acid in suspension.

A reinvestigation of the composition of the carbonyl<sup>3</sup> has shown that it is more exactly represented by the formula  $\text{Mo}_5(\text{CO})_{26}$ . The substance is only slightly soluble in benzene, alcohol, and other common solvents, so that cryoscopic determinations of its molecular weight could not be made.

#### MOLYBDENUM AND CYANOGEN.

The simple cyanides of molybdenum do not appear to have been isolated, but a large number of complex compounds have been described. It was observed by Péchard<sup>4</sup> that molybdenum dioxide dissolves in aqueous potassium cyanide forming a strongly alkaline blue liquid, which on concentration deposits blue needles, to which he gave the formula  $\text{MoO}_2(\text{CN})_2 \cdot 2\text{KCN}$ . The compound is readily soluble in water, and gives with solutions of metallic salts characteristically coloured precipitates: bluish white with lead, pale brown with copper, greenish blue with mercuric salts, and dark brown with silver salts. Several complex compounds, apparently containing tetravalent molybdenum, may be obtained<sup>5</sup> by reduction of potassium molybdate in presence of potassium cyanide. For example, by reduction with hydroxylamine hydrochloride, violet crystals, of composition  $\text{MoO}_2 \cdot 4\text{KCN} \cdot \text{NH}_2\text{OH} + \text{H}_2\text{O}$ , are obtained, while on neutralising a solution of the oxychloride,

<sup>1</sup> Hilpert and Ornstein, *Ber.*, 1913, 46, 1669.

<sup>2</sup> Mond, Hirtz, and Cowap, *Trans. Chem. Soc.*, 1910, 97, 798.

<sup>3</sup> Mond and Wallis, *ibid.*, 1922, 121, 29.

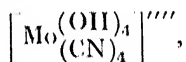
<sup>4</sup> Péchard, *Compt. rend.*, 1894, 118, 804.

<sup>5</sup> Heide and Hofmann, *Zeitsch. anorg. Chem.*, 1896, 12, 277.

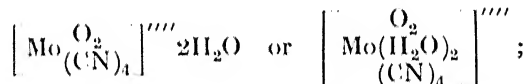
$\text{MoOCl}_3$ , with potassium hydroxide and adding excess of potassium cyanide, a blue solution results which, on further addition of potassium hydroxide, yields a bluish-red crystalline precipitate, of composition  $\text{MoO}_2 \cdot 4\text{KCN} \cdot 10\text{H}_2\text{O}$ . This compound may also be obtained<sup>1</sup> by the addition of a large excess of potassium cyanide to an aqueous solution of the compound  $\text{Mo}(\text{OH})_2(\text{SCN})_3 \cdot 2\text{C}_5\text{H}_5\text{N}$  (see below); when only a slight excess of potassium cyanide was used, the compound  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  was obtained in yellow plates. The latter compound was first obtained<sup>2</sup> by the action of potassium cyanide on the double chloride of potassium and molybdenum; it is readily soluble in water, and is stable towards acids and dilute alkalis. When the aqueous solution is exposed to direct sunlight, its colour changes to red and then to pale green, hydrogen cyanide being formed.

The composition of this compound is particularly interesting, since it was recognised as the first compound with a stable complex ion of which the co-ordination number was greater than 6. The valency of the molybdenum present was for some time in doubt,<sup>3</sup> for whilst the empirical formula suggested that the metal should be tetravalent, titration with permanganate indicated that it was in the pentavalent condition; it was shown by Olsson,<sup>4</sup> however, that permanganate oxidised the compound, not to molybdic acid, but to a complex cyanide of the type  $\text{R}_3\text{Mo}(\text{CN})_8$ , in which the molybdenum is pentavalent. Olsson was unable to isolate this compound, but he arrived at his conclusions through the analogous tungsten compounds, and he did succeed in isolating the salts of this metal of the type  $\text{R}_3\text{W}(\text{CN})_8 \cdot x\text{H}_2\text{O}$  (see p. 262).

Two definite series of complex molybdocyanides, containing tetra-valent molybdenum, are now recognisable:<sup>5</sup> (1) the reddish-violet salts containing the complex anion



which on evaporation with water are converted to blue salts containing the anion



and (2) the yellow salts, obtained by the action of alkali cyanides on the blue salts, of the type  $\text{R}_4[\text{Mo}(\text{CN})_8]$ .

**Reddish-violet Salts.** The potassium salt,  $[\text{Mo}(\text{OH})_4(\text{CN})_4]$   $\text{K}_4 \cdot 6\text{H}_2\text{O}$ , described above as  $\text{MoO}_2 \cdot 4\text{KCN} \cdot 10\text{H}_2\text{O}$ , yields reddish-violet monoclinic tables:

$$a : b : c = 0.7324 : 1 : 0.5723.$$

The difference in water content, shown in the latter formula, is due to insufficient drying; if dried over sulphuric acid the salt has the composition<sup>6</sup>  $[\text{MoO}_2(\text{CN})_4] \cdot \text{K}_4 \cdot 6\text{H}_2\text{O}$ .

<sup>1</sup> Rosenheim and Koss, *Zeitsch. anorg. Chem.*, 1906, **49**, 148.

<sup>2</sup> Chilesotti, *Gazzetta*, 1904, **34**, [2], 493.

<sup>3</sup> Rosenheim, Garfunkel, and Kohn, *Zeitsch. anorg. Chem.*, 1909, **65**, 166; Rosenheim, *ibid.*, 1910, **66**, 95.

<sup>4</sup> Olsson, *Ber.*, 1914, **47**, 917. See also Rosenheim and Dehn, *ibid.*, 1915, **48**, 1167; Collenberg, *Zeitsch. anorg. Chem.*, 1922, **121**, 298.

<sup>5</sup> Rosenheim, Garfunkel, and Kohn, *loc. cit.*

<sup>6</sup> Winkler, *Dissertation*, Zurich, 1909.

The *sodium* salt,  $[\text{Mo}(\text{OH})_4(\text{CN})_4] \cdot 12\text{H}_2\text{O}$ , is similar to the potassium salt, and yields  $[\text{MoO}_2(\text{CN})_4][\text{Na}_4 \cdot 6\text{H}_2\text{O}]$  when dried over sulphuric acid.

**Yellow Salts.**—The acid from which these salts are derived, molybdoeyanic acid,  $\text{H}_4\text{Mo}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$ , has been prepared<sup>1</sup> by adding hydrochloric acid, of density 1.19, to a concentrated solution of the potassium salt (see below), extracting the precipitate with alcohol, and precipitating with ether in a freezing mixture. It forms yellow needles, readily soluble in water and alcohol, the solutions being stable and yielding on neutralisation with bases the corresponding salts.

The *potassium* salt,  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ , first obtained by Chilesotti, as already described, yields yellow rhombic-bipyramidal crystals :

$$a : b : c = 0.7028 : 1 : 0.3711.2$$

When heated to  $110^\circ \text{C}$ . it loses its water of crystallisation. It is readily soluble in water.

The *cadmium* salt,  $\text{Cd}_2\text{Mo}(\text{CN})_8 \cdot 8\text{H}_2\text{O}$ , forms light yellow microscopic needles, insoluble in water, soluble in ammonia.

The *manganese* salt,  $\text{Mn}_2\text{Mo}(\text{CN})_8 \cdot 8\text{H}_2\text{O}$ , yields bright yellow glistening leaflets.

The *thallium* salt,  $\text{Tl}_4\text{Mo}(\text{CN})_8$ , occurs in long, lustrous, reddish-yellow needles, slightly soluble in water.

The *pyridinium* salt has also been described.<sup>4</sup>

**Metal-ammine** salts have also been obtained by Rosenheim and his co-workers by dissolving the molybdicyanides in boiling concentrated ammonia and allowing to crystallise: the cadmium-ammine,  $\text{Cd}_2(\text{NH}_3)_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ , deep yellow needles; the copper-ammine,  $\text{Cu}_2(\text{NH}_3)_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ , deep green needles; the nickel-ammine,  $[\text{Ni}(\text{NH}_3)_4]_2\text{Mo}(\text{CN})_8 \cdot 8\text{H}_2\text{O}$ , bluish-grey needles; and the silver-ammine,  $\text{Ag}_4(\text{NH}_3)_8\text{Mo}(\text{CN})_8$ , lustrous yellow needles. It is probable that the last-named salt has 4 molecules of  $\text{NH}_3$  when first formed.

**Thiocyanates of Molybdenum.**—Thiocyanates containing molybdenum as a cation are not known, but compounds similar to the complex cyanides, in which the metal figures as the central atom of a complex anion, have been prepared.

1. Compounds containing trivalent molybdenum of the type  $\text{R}_3[\text{Mo}(\text{SCN})_6] \cdot x\text{H}_2\text{O}$ .<sup>3</sup> Many salts which appear to be of this type have been prepared by Sand and Maas, who formulate them with  $(\text{OH})$  or  $(\text{H}_2\text{O})$  of constitution thus:  $[\text{Mo}(\text{SCN})_6 \cdot \text{OH}]\text{R}_3 \cdot x\text{H}_2\text{O}$  and  $[\text{Mo}(\text{SCN})_6 \cdot \text{H}_2\text{O}]\text{R}_3 \cdot x\text{H}_2\text{O}$ .<sup>4</sup> The *potassium* salt,  $\text{K}_3\text{Mo}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$ , may be prepared by the action of potassium thiocyanate on the double chloride,  $\text{K}_3\text{MoCl}_6$ . It yields orange-coloured crystals, readily soluble in water, and which readily lose water of crystallisation, becoming dark red in colour or, if heated to complete dehydration, almost black. The method of preparation used by Sand and Maas involved the electrolysis of potassium molybdate and thiocyanate in hydrochloric acid solution. The sodium and ammonium salts may be obtained by either of the two

<sup>1</sup> Rosenheim, Garfunkel, and Kohn, *Zeitsch. anorg. Chem.*, 1909, **65**, 166.

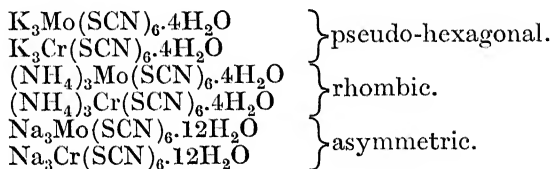
<sup>2</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1907, **54**, 97, where electrical conductivity and freezing-point data for solutions of this salt are also given.

<sup>3</sup> Chilesotti, *Gazzetta*, 1904, **34**, [2], 493; Sand and Burger, *Ber.*, 1906, **39**, 1761; Sand and Maas, *ibid.*, 1907, **40**, 4504; 1908, **41**, 1500, 1861, 3367; 1909, **42**, 2642; Rosenheim and Garfunkel, *ibid.*, 1908, **41**, 2386; Rosenheim, *ibid.*, 1909, **42**, 149, 2295.

<sup>4</sup> See also Scagliarini and Tartarini, *Gazzetta*, 1923, **53**, 876.

methods described, while insoluble salts of copper, nickel, silver, and zinc are obtained by addition of solutions of these metals to a solution of the complex alkali salt. Many metal-ammine derivatives and compounds with organic bases have been described.

The alkali hexathiocyanates are not isomorphous amongst themselves, but each molybdenum salt is isomorphous with the corresponding chromium salt (see p. 99) thus :



The thallium salt,  $\text{Tl}_3\text{Mo}(\text{SCN})_6$ , is formed as an amorphous, light yellow precipitate when thallium nitrate is added to a solution of the potassium salt.

The molybdenum in these salts may be oxidised by ammoniacal silver nitrate and the equivalent of the molybdenum calculated from the amount of silver liberated; the results obtained indicate a trivalent molybdenum atom.

2. Compounds containing tetravalent molybdenum. When precipitated molybdenum disulphide is dissolved in a warm solution of potassium cyanide, a deep green liquid is formed which on concentration yields <sup>1</sup> slender black needles of composition  $\text{MoS}_2(\text{CN})_2 \cdot 2\text{KCN}$ . The compound is also obtained by boiling a solution of potassium thiomolybdate with an excess of potassium cyanide until the red colour completely changes to green. When heated with acids it yields hydrocyanic acid and molybdenum disulphide. The green solution is precipitated with alcohol, a greenish oil separating which gradually solidifies. An examination of the reaction between potassium cyanide and molybdenum disulphide suggests <sup>2</sup> that three different compounds may be formed according to the length of time allowed for the reaction, namely,  $\text{Mo}_2\text{S}_3 \cdot 6\text{KCN} \cdot 5\text{H}_2\text{O}$ , which forms green silky crystals when the action goes for a short time;  $\text{Mo}_2\text{SO}(\text{CN})_2 \cdot 4\text{KCN} \cdot 4\text{H}_2\text{O}$ , obtained as beautiful reddish-brown needles by evaporating the reacting mixture in a vacuum; and  $\text{Mo}_3\text{S}_4(\text{CN})_3 \cdot 5\text{KCN} \cdot 7\text{H}_2\text{O}$ , which results in large black crystals (green by transmitted light) on allowing the preceding salt to remain in contact with the mother-liquor over sulphuric acid. The mode of formation and the properties of these compounds indicate the presence of tetravalent molybdenum, but in order to establish their true nature further investigation is desirable.

3. Compounds containing pentavalent molybdenum. When a solution of ammonium molybdate and ammonium thiocyanate is reduced electrolytically and the resulting liquid extracted with ether, all the red-colouring substances pass into the latter; on adding pyridine, a compound, of composition  $\text{Mo}(\text{OH})_2(\text{SCN})_3(\text{C}_5\text{H}_5\text{N})_2$ , is obtained <sup>3</sup> in the

<sup>1</sup> Péchard, *Compt. rend.*, 1894, 118, 804.

<sup>2</sup> Heide and Hofmann, *Zeitsch. anorg. Chem.*, 1896, 12, 277.

<sup>3</sup> Sand and Burger, *Ber.*, 1905, 38, 3384; 1906, 39, 1761. See also Braun (*Zeitsch. anal. Chem.*, 1863, 2, 36; 1867, 6, 86; *J. prakt. Chem.*, 1863, 89, 125), Kalischer (*Dissertation*, Berlin, 1902), Rosenheim and Koss (*Zeitsch. anal. Chem.*, 1906, 49, 148), for a discussion of this and similar compounds.

form of dark brownish-red feathery aggregates of crystals, which may be recrystallised from hot alcohol, and which melt and decompose at  $182^{\circ}\text{C}$ . Similar compounds with other organic bases have been described.

### MOLYBDENUM AND SILICON.

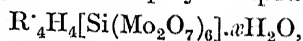
Three silicides of molybdenum have been described, but only one, the disilicide  $\text{MoSi}_2$ , has been definitely established as a true compound.

**Molybdenum Monosilicide,  $\text{MoSi}$ ,** is formed <sup>1</sup> when the metal is heated with amorphous silicon in a vacuum to  $1100^{\circ}$  to  $1200^{\circ}\text{C}$ . The product is unattacked by acids.

**Molybdenum Sesquisilicide,  $\text{Mo}_2\text{Si}_3$ ,** is said <sup>2</sup> to result when crystallised silicon is heated in a carbon crucible in the electric furnace with the oxides of molybdenum obtained by calcining ammonium molybdate. The mass is disintegrated by electrolysis in hydrochloric acid, and the residue successively treated with aqua regia, caustic alkali, and hydrofluoric acid. The silicide burns in chlorine at  $300^{\circ}\text{C}$ ., with formation of silicon tetrachloride and molybdenum pentachloride.

**Molybdenum Disilicide,  $\text{MoSi}_2$ ,** may be prepared <sup>3</sup> by heating a mixture of the oxides of molybdenum, silicon, and boron with metallic copper and aluminium in an arc furnace, cryolite being added as a flux and lime as a retarder to prevent the reaction becoming too violent; by heating a mixture of copper silicide, containing 50 per cent. silicon, and amorphous molybdenum in an electric furnace; <sup>4</sup> or by igniting a mixture of molybdic anhydride, powdered aluminium, flowers of sulphur, and fine sand in a Hessian crucible by the Goldschmidt aluminothermic method.<sup>5</sup> Molybdenum disilicide crystallises in lustrous iron-grey prisms, of density <sup>6</sup> 6.31 at  $20.5^{\circ}\text{C}$ . It remains unchanged when heated in air or in oxygen, and is very resistant to acids, although it readily dissolves in a mixture of nitric and hydrofluoric acids. It reacts with fluorine at ordinary temperatures, with chlorine at about  $400^{\circ}\text{C}$ ., and slowly with bromine in presence of hydrogen at a red heat; it also dissolves in fused alkalis, and in mixtures of these with alkali nitrates and chlorates.

**Molybdosilicic Acid and Molybdosilicates.**—When a boiling solution of sodium silicate is saturated with molybdic acid it becomes intensely yellow, and on evaporation at  $45^{\circ}\text{C}$ . deposits yellow crystals of composition  $2\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 21\text{H}_2\text{O}$ .<sup>7</sup> The compound may also be obtained by heating a mixture of sodium silicate and molybdic acid with a little water in a sealed tube at  $150^{\circ}\text{C}$ .,<sup>8</sup> or by addition of hydrofluosilicic acid, or sodium silicofluoride, to an acidified solution of sodium molybdate. By these methods, or by double decomposition, numerous salts have been prepared, and they are considered by Rosenheim to belong to a type of heteropoly-compounds of general formula



<sup>1</sup> Wedekind and Pintsch, *German Patent*, 294267 (1916).

<sup>2</sup> Vigouroux, *Compt. rend.*, 1899, 129, 1238.

<sup>3</sup> Watts, *Trans. Amer. Electrochem. Soc.*, 1906, 9, 105.

<sup>4</sup> Defacqz, *Compt. rend.*, 1907, 144, 1424.

<sup>5</sup> Hönigschmid, *Monatsh.*, 1907, 28, 1017.

<sup>6</sup> Watts, *loc. cit.* See also Defacqz (*loc. cit.*) and Hönigschmid (*loc. cit.*).

<sup>7</sup> Asch, *Zeitsch. anorg. Chem.*, 1901, 28, 273.

<sup>8</sup> Copaux, *Ann. Chim. Phys.*, 1906, [8], 7, 118. See also Parmentier, *Compt. rend.*, 1881, 92, 1234; 1882, 94, 213.

being acid salts of an octobasic acid.<sup>1</sup> Salts of practically all the common metals have been prepared.<sup>2</sup> Many of them form different hydrates, and they are usually isomorphous with the corresponding silicotungstates. The sodium and alkaline earth salts are readily soluble in water, the potassium and ammonium salts are less soluble, while the mercurous, thallium, and rubidium salts are very sparingly soluble.

**12-Molybdosilicic Acid**,  $H_8[Si(Mo_2O_7)_6] \cdot 28H_2O$ , is prepared by decomposing the sodium salt with dilute sulphuric acid and extracting with ether.<sup>3</sup> It yields transparent octahedra<sup>4</sup> which melt at  $47^\circ$  to  $55^\circ$  C. to a uniform liquid. Crystallised from hot nitric acid it yields a lower hydrate with  $14H_2O$ .

When an alkali chloride or nitrate is added to a solution of the acid, or when solutions of the tetrabasic salts are treated with hydrochloric acid, yellow salts of formula  $R'_3H_5[Si(Mo_2O_7)_6] \cdot xH_2O$  ( $R' = Na, K, Ag$ ) are obtained. Attempts to produce the normal alkali and guanidinium salts have not been successful, but on addition of concentrated silver or mercurous nitrate solutions to a solution of the tetrabasic sodium salt, yellow crystalline precipitates, of composition  $Ag_8[Si(Mo_2O_7)_6] \cdot 15H_2O$  and  $Hg_8[Si(Mo_2O_7)_6]$ , are obtained.<sup>5</sup>

Compounds containing vanadium, of the type  $R'_6H_2[Si(Mo_2O_7)_5(V_2O_6)] \cdot xH_2O$ , have been described.<sup>6</sup>

#### MOLYBDENUM AND BORON.

When molybdenum and boron are heated together in the electric furnace crystalline borides are produced. By heating a mixture containing 6 grams of metallic molybdenum, obtained by reduction of the trioxide and 1 gram of boron, Tucker and Moody<sup>7</sup> obtained a homogeneous product which was free from carbon and silicon. It was crystalline in structure, of hardness 9 and of density 7.105. It was quite brittle, and on fracture showed a brilliant metallic lustre similar to that of pale brass. Hot concentrated acids attacked it slowly, but hot aqua regia acted more vigorously. Analysis showed the presence of 86 per cent. of molybdenum, and the formula  $Mo_3B_4$ , which requires 86.7 per cent. Mo, was suggested. These experiments, however, were repeated by Wedekind,<sup>8</sup> who obtained a product containing 88 per cent. of molybdenum and 9.9 per cent. of boron, so that the molybdenum content was too high to agree with the above formula, especially in view of the fact that the boride contained impurities. Wedekind also produced an impure boride, having the approximate composition  $Mo_2B$ , by passing an arc between electrodes (made by submitting mixtures of finely powdered molybdenum and boron to hydraulic pressure) in a

<sup>1</sup> Miolati and Pizzighelli, *J. prakt. Chem.*, 1908, [2], 77, 417; Rosenheim and Pinsker, *Zeitsch. anorg. Chem.*, 1911, 70, 73.

<sup>2</sup> For properties and crystallographic data of these salts, see Copaux (*loc. cit.*) and Asch (*loc. cit.*).

<sup>3</sup> Asch, *loc. cit.*; Drechsel, *Ber.*, 1887, 20, 1452. See also Parmentier, *Compt. rend.*, 1882, 94, 213.

<sup>4</sup> Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1917, 101, 235.

<sup>5</sup> Asch, *loc. cit.*

<sup>6</sup> Friedheim and Custendyck, *Ber.*, 1900, 33, 1611.

<sup>7</sup> Tucker and Moody, *Trans. Chem. Soc.*, 1902, 81, 14.

<sup>8</sup> Wedekind and Jochem, *Ber.*, 1913, 46, 1198.

vacuum electrical furnace; the heat brought about the formation of the boride with disintegration of the electrodes.

Non-crystalline alloys of molybdenum and boron have been obtained<sup>1</sup> by heating together molybdenum dioxide and boron in magnesia crucibles. These alloys, containing up to 46 per cent. of boron, decrease in density and increase in hardness with increase in the percentage of boron. They are not attacked by hydrochloric and hydrofluoric acids or by alkalis, but concentrated sulphuric acid acts on warming, and dilute nitric acid dissolves them in the cold.

#### DETECTION AND ESTIMATION OF MOLYBDENUM.

Molybdenum most frequently occurs in the hexavalent state in derivatives of the trioxide  $\text{MoO}_3$ , this being the fully oxidised condition and its most stable form. The lower oxides and their salts can readily be oxidised to molybdates, and this is usually done before the metal is estimated.

**Detection: Dry Tests.**—When mixed with fusion mixture and heated on carbon in a reducing flame, molybdenum compounds yield a blue or dark red incrustation. The borax bead gives a brown colour when hot, which becomes green on cooling, but more distinct colours are obtained with a bead of microcosmic salt. Molybdenum compounds impart a faint yellowish-green colour to the Bunsen flame. Traces of molybdic acid and its compounds may be detected<sup>2</sup> in a powder by adding a few particles of the latter to a drop of sulphuric acid on a platinum foil or on porcelain and heating until thick fumes are evolved; on cooling and moistening the residue with the breath, an intense blue<sup>3</sup> colour appears, which vanishes on heating but reappears on cooling. The colour is permanently destroyed if water is added.

**Wet Tests.**—When hydrogen sulphide is passed through an acidified solution containing molybdenum, the trisulphide is thrown down. The precipitate dissolves in ammonium sulphide, and it is therefore in ordinary analysis separated with the Group IIB metals, namely, arsenic, antimony, tin, gold, and platinum. The last four metals may be precipitated by addition of metallic zinc,<sup>4</sup> the arsenic expelled by evaporation, and, after taking to dryness with nitric acid, the molybdenum may be extracted from the residue with ammonia. The trisulphide may be reprecipitated directly by the addition of nitric acid to the solution in ammonium sulphide. A soluble sulphide added to a solution of ammonium molybdate gives a blue colour.

Various colour effects are obtained by the addition of reducing agents to solutions of molybdenum compounds. Zinc in the presence of acid,<sup>5</sup> and stannous chloride, produce colours changing from blue to green, brown, and yellow. Sulphur dioxide produces a bluish-green coloration or precipitate according to the amount of molybdenum present. A

<sup>1</sup> du Jassonneix, *Compt. rend.*, 1906, 143, 169.

<sup>2</sup> Truchot, *Ann. Chim. anal.*, 1905, 10, 254; Maschke, *Zeitsch. anal. Chem.*, 1873, 12, 383; Schön, *ibid.*, 1869, 8, 379.

<sup>3</sup> In presence of vanadium the colour is more or less green.

<sup>4</sup> For alternative separations the reader should consult standard works on analysis. For the separation of Pt, As, Au, Se, Te, and Mo, see Browning, *Amer. J. Sci.*, 1915, [4], 40, 349. For the separation of As from V and Mo, e.g. in arseno-vanadio molybdates, see Friedheim, Decker, and Diem, *Zeitsch. anal. Chem.*, 1905, 44, 665.

<sup>5</sup> Reichard, *Chem. Zeit.*, 1903, 27, 1.

blue precipitate is also obtained when sodium thiosulphate is added to a slightly acid solution of ammonium molybdate.

Precipitation reactions with ordinary reagents are not very characteristic. A neutral solution of molybdate gives with silver nitrate a white, curdy precipitate soluble in ammonia or nitric acid, and with barium chloride a white precipitate soluble in hydrochloric acid. Disodium hydrogen phosphate added to a solution of ammonium molybdate gives a yellow precipitate of ammonium 12-molybdophosphate (see p. 164) insoluble in nitric acid, soluble in ammonia.

Numerous *colour reactions* for the detection of molybdenum have been described, some of which are extremely sensitive. Hydrogen peroxide gives a yellow colour with a molybdate in presence of sulphuric acid; <sup>1</sup> if the solution is first evaporated and the residue treated with concentrated ammonia before adding the hydrogen peroxide, a cherry-red or pale rose coloration, due to the formation of ammonium permolybdate, is obtained.<sup>2</sup> A delicate test for molybdenum in presence of mercury consists in precipitating mercurous iodide by means of potassium iodide <sup>3</sup> and redissolving the precipitate in excess of the reagent, whereupon reduction to mercury takes place which in its turn reduces the molybdate and the supernatant liquid turns blue. Very dilute solutions of molybdates are not affected. The blue colour may be obtained with tungstates, although the test is of little value for their detection; in order to determine whether the blue colour is due to molybdenum or tungsten, potassium thiocyanate should be added, when, if the former is present, the blue colour turns to blood-red. In a similar manner reduction of a molybdate by means of zinc in presence of thiocyanate yields a crimson colour; if iron is present, the red colour first produced disappears as reduction proceeds and the crimson for molybdenum develops.<sup>4</sup> When a solution of a molybdate containing an alkali thiocyanate is treated with concentrated hydrochloric or sulphuric acid, a purple colour is produced,<sup>5</sup> while, if instead of the mineral acid acetic acid is used, the colour is yellow,<sup>6</sup> and if the solution is concentrated, yellow acicular crystals, of composition <sup>7</sup>  $R \cdot SCN \cdot R' \cdot 0.4MoO_3 \cdot 5H_2O$  ( $R=K, NH_4$ ), separate. Reduction of a molybdate by means of stannous chloride in presence of a thiocyanate, and extraction of the red compound formed by means of ether, affords an extremely delicate test for traces of molybdenum, 1 part of molybdenum in 625,000 parts of water being readily detected.<sup>8</sup>

Similar colour reactions to the above are based on the reducing action of certain organic compounds. For example, a solution of an alkali molybdate in acetic acid gives <sup>9</sup> an orange colour with pyrogallol or pyrocatechol, and a deep blue colour with quinol or hydrazine, while

<sup>1</sup> Werther, *J. prakt. Chem.*, 1861, 83, 195; Schönn, *Zeitsch. anal. Chem.*, 1870, 9, 41.

<sup>2</sup> Melikoff, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 608; Komarowsky, *Chem. Zeit.*, 1913, 37, 957; Bettel, *Chem. News*, 1908, 97, 40.

<sup>3</sup> Kafka, *Zeitsch. anal. Chem.*, 1912, 51, 482; Pozzi-Escot, *Bull. Soc. chim.*, 1913, [4], 13, 402, 1042.

<sup>4</sup> Moir, *J. Chem. Metall. Min. Soc. S. Africa*, 1916, 16, 191.

<sup>5</sup> Braun, *Zeitsch. anal. Chem.*, 1863, 2, 36; 1867, 6, 86; *J. prakt. Chem.*, 1863, 89, 125.

<sup>6</sup> Péchard, *Compt. rend.*, 1894, 118, 804.

<sup>7</sup> Barbieri, *Atti R. Accad. Lincei*, 1919, [5], 28, i, 351, 390.

<sup>8</sup> Štěrbá-Böhm and Votrěbal, *Zeitsch. anorg. Chem.*, 1920, 110, 81.

<sup>9</sup> Moir, *loc. cit.* See also Weinland and Gaisser, *Zeitsch. anorg. Chem.*, 1919, 108, 231; Weinland and Zimmermann, *ibid.*, 1919, 108, 248; Weinland and Huthmann, *Arch. Pharm.*, 1924, 262, 329.



with excess of phenylhydrazine a red colour is obtained.<sup>1</sup> An alcoholic solution of diphenylcarbazine gives an indigo-violet colour when added to a slightly acid solution of a molybdate, a violet precipitate being formed with excess of the reagent;<sup>2</sup> tungsten, vanadium, and titanium give no reaction. Tannin gives an orange coloration when added to a neutral solution of molybdic acid,<sup>3</sup> which becomes cherry-red in concentrated, and yellow in dilute, solutions. The colour is not altered by boiling, but is destroyed by the addition of acids.

One of the most sensitive reagents for molybdenum is xanthic acid. It was first observed by Siewert<sup>4</sup> that this reagent gave a characteristic red colour with molybdenum compounds. To a freshly prepared xanthate solution, made by shaking a solution of potassium hydroxide in absolute alcohol with excess of carbon disulphide until no more of the latter dissolves, a 30 per cent. solution of acetic acid is added until a slight yellow turbidity appears. This solution is added drop by drop to the solution to be tested, and if molybdenum is present a red colour develops, the intensity of which is proportional to the amount of molybdenum present.<sup>5</sup> The test is capable of detecting 0.0000064 gram of molybdenum per c.c., and is not affected by the presence of vanadium, tungsten, titanium, or uranium, so that it may be used for detecting the element in iron and steel. Chromates give a dark colour with xanthic acid, and should therefore be first reduced if present.

**Estimation of Molybdenum.**—In the analysis of molybdenum ores, a solution is best obtained by fusion with sodium carbonate and potassium nitrate and extraction with hydrochloric acid. In the case of iron and steel, the metal may be dissolved in a mixture of hydrochloric and nitric acids with gentle heating so that the iron is oxidised. Sufficient sodium hydroxide is then added to precipitate the iron and to dissolve the molybdic acid on heating. After cooling, the alkali is neutralised with hydrochloric acid, and the molybdenum may then be estimated by one of the methods to be described.<sup>6</sup>

**Gravimetric Methods.**—The metal is conveniently precipitated from solution as lead molybdate<sup>7</sup> by means of lead acetate in presence

<sup>1</sup> Spiegel and Maass, *Ber.*, 1903, 36, 512; Pozzi-Escot, *Ann. Chim. anal.*, 1907, 12, 92.

<sup>2</sup> Lecocq, *Chem. Zentr.*, 1904, i, 836.

<sup>3</sup> Pozzi-Escot, *Compt. rend.*, 1904, 138, 200.

<sup>4</sup> Siewert, *Zeitsch. ges. Naturwiss.*, 1864, 23, 5.

<sup>5</sup> Malowan, *Zeitsch. anorg. Chem.*, 1919, 108, 73; Koppel, *Chem. Zeit.*, 1919, 43, 777.

<sup>6</sup> For recent work on the analysis of molybdenum ores, see Hoepfner and Binder, *Chem. Zeit.*, 1918, 42, 315, 564; Tancy, *Met. and Chem. Eng.*, 1918, p. 186; Trautmann, *Zeitsch. angew. Chem.*, 1911, 24, 207; *Chem. Zeit.*, 1909, 33, 1106; Collet and Eckhardt, *ibid.*, 1909, 33, 968; Gilbert, *Zeitsch. öffentl. Chem.*, 1906, 12, 263. For the estimation of molybdenum in iron and steel, see Travers, *Compt. rend.*, 1917, 165, 362; Armstrong, *J. Ind. Eng. Chem.*, 1915, 7, 764; Zinberg, *Zeitsch. anal. Chem.*, 1913, 52, 529; Trautmann, *ibid.*, 1910, 49, 360; Müller and Diethelm, *Zeitsch. angew. Chem.*, 1910, 23, 2114; Blair, *J. Amer. Chem. Soc.*, 1908, 30, 1229; Auchy, *ibid.*, 1905, 27, 1240; 1903, 25, 215; van Dyke, Cruser, and Miller, *ibid.*, 1904, 26, 675. For the recovery of molybdenum from residues from steel analysis and from filtrates from phosphorus estimations, see Prescott, *Analyst*, 1915, 40, 390; Kinder, *Stahl und Eisen*, 1916, 36, 1094; *Chem. Zentr.*, 1917, i, 530; Armstrong, *loc. cit.*; Rudnick and Cooke, *J. Ind. Eng. Chem.*, 1917, 9, 109; Lenher and Schultz, *ibid.*, 1917, 9, 684; Friedrich, *Chem. Zeit.*, 1916, 40, 560; 1917, 41, 674; Malowan, *ibid.*, 1918, 42, 410; Lynas, *Met. and Chem. Eng.*, 1918, p. 169; Neubauer and Wolferts, *Zeitsch. anal. Chem.*, 1919, 58, 445.

<sup>7</sup> Chatard, *Amer. J. Sci.*, 1871, [3], 1, 416; Weiser, *J. Physical Chem.*, 1916, 20, 640; Streibinger, *Oesterr. Chem. Zeit.*, 1918, [2], 20, 226; Congdon and Rohner, *Chem. News*, 1924, 128, 118.

of acetic acid. The precipitate is granular, and, after washing with hot water, is dried, ignited, and weighed as  $\text{PbMoO}_4$ . By this means molybdenum may be completely separated, if the solution is sufficiently acid, from copper, cadmium, mercury, arsenic, phosphorus, iron, aluminium, chromium, zinc, manganese, nickel, cobalt, calcium, barium, strontium, magnesium, or uranium, but vanadium or tungsten, if present, must first be removed. Molybdenum may also be precipitated as the trisulphide, and the precipitate ignited and weighed as the trioxide,  $\text{MoO}_3$ .<sup>1</sup> The conversion of the sulphide to the trioxide is complete at about  $400^\circ \text{C}$ ., and above  $450^\circ \text{C}$ . the trioxide sublimes; the temperature must therefore be maintained at  $400^\circ$  to  $425^\circ \text{C}$ ., and this is best done by using the electric furnace. If the ore under examination has been fused with alkali carbonate and the alkali molybdate extracted, a suitable method of estimation is the precipitation of the molybdenum as mercurous molybdate by means of mercurous nitrate, the precipitate then being converted to the trioxide by gentle ignition. If chromium, vanadium, tungsten, arsenic, or phosphorus are present, these elements will also be precipitated, so that a separation should first be effected.<sup>2</sup>

A method, suitable for the analysis of molybdates and molybdenum ores, consists in heating the substance at  $400^\circ$  to  $560^\circ \text{C}$ . in a stream of carbon tetrachloride vapour,<sup>3</sup> when molybdic acid volatilises and may be collected in a receiver, evaporated with nitric acid, ignited, and weighed. If iron is present it also volatilises, and must be separated from the condensed product.

**Volumetric Methods.** Molybdic acid and soluble molybdates, when boiled with potassium iodide in presence of hydrochloric acid, are reduced, while free iodine is liberated according to the equation <sup>4</sup>



The iodine may be estimated by means of a standard thiosulphate solution, or by shaking with specially prepared electrolytic silver <sup>5</sup> in an atmosphere of hydrogen, and measuring the increase in weight of the silver; or, after removing the iodine by boiling, the molybdenum in the reduced solution may be directly estimated by reoxidation in alkaline solution by means of standard iodine or potassium permanganate.

Other methods are similarly based on the reduction of molybdic acid; for example, by means of zinc,<sup>6</sup> magnesium,<sup>7</sup> or sulphur dioxide,<sup>8</sup> the resulting solution then being titrated with standard potassium per-

<sup>1</sup> Binder, *Chem. Zeit.*, 1918, 42, 255; Wolf, *Zeitsch. angew. Chem.*, 1918, 31, i., 140; Trautmann, *ibid.*, 1910, 23, 1981; Störba-Böhm and Vostřebal, *loc. cit.*

<sup>2</sup> For other methods, see Jannasch and Laubi, *J. prakt. Chem.*, 1918, [2], 97, 154; Jannasch and Bettges, *Ber.*, 1904, 37, 2219. On the separation of molybdenum and tungsten, see Marbaker, *J. Amer. Chem. Soc.*, 1915, 37, 86; Merrill, *ibid.*, 1921, 43, 2383; Hall, *ibid.*, 1922, 44, 1462; King, *J. Ind. Eng. Chem.*, 1923, 15, 350; Koppel, *Chem. Zeit.*, 1924, 48, 801.

<sup>3</sup> Jannasch and Laubi, *J. prakt. Chem.*, 1918, [2], 97, 154.

<sup>4</sup> Perkins, *Amer. J. Sci.*, 1910, [4], 29, 540; *Zeitsch. anorg. Chem.*, 1910, 67, 361; Gooch and Pulman, *Amer. J. Sci.*, 1901, [4], 12, 449; Gooch and Fairbanks, *ibid.*, 1896, [4], 2, 160.

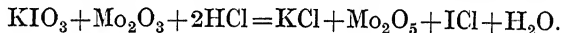
<sup>5</sup> Perkins, *loc. cit.*

<sup>6</sup> Noyes and Frohman, *J. Amer. Chem. Soc.*, 1913, 35, 919; Reinhardt, *Chem. Zeit.*, 1889, 13, 33; Knecht and Atack, *Analyst*, 1911, 36, 98; Scott, *J. Ind. Eng. Chem.*, 1920, 12, 578; Nakazono, *J. Chem. Soc. Japan*, 1921, 42, 526.

<sup>7</sup> Glassmann, *Ber.*, 1905, 38, 604.

<sup>8</sup> Edgar, *Amer. J. Sci.*, 1908, [4], 25, 332.

manganate.<sup>1</sup> The Jones reductor is most generally used,<sup>2</sup> the molybdic acid solution being passed through a column of amalgamated zinc into a solution of ferric alum. In the absence of titanium, tungsten, chromium, and vanadium, the reduced solution may be titrated with a standard solution of methylene blue.<sup>3</sup> The solution of ferric alum may be replaced by hydrochloric acid containing iodine monochloride solution and chloroform,<sup>4</sup> the liquid then being titrated with potassium iodate solution, when the reaction proceeds according to the equation



Small quantities of molybdenum may be determined<sup>5</sup> by reduction with excess of titanous chloride, and titrating back with ferric chloride solution, potassium thiocyanate being used as indicator; or the reduction may be followed electrometrically.<sup>6</sup> If tungsten is present it must be eliminated by precipitation before the addition of the reducing agent.

**Colorimetric Method.**—Molybdenum may be detected quantitatively by means of the xanthic acid test already described (p. 178). The red product is extracted with a mixture of ether and light petroleum (65 : 35) and the extract diluted with another mixture of ether and light petroleum (80 : 70) for comparison with the standard solution.<sup>7</sup> If pure ether is used, decomposition takes place.

**Electrolytic Methods.**—Molybdenum may be accurately determined in solutions of molybdates by means of electrolysis.<sup>8</sup> In presence of free sulphuric acid the metal is completely precipitated on the cathode as the hydrated sesquioxide. Hydrochloric acid may be used<sup>9</sup> instead of sulphuric acid to accelerate the deposition. The precipitate after washing may be converted by gentle ignition to molybdenum trioxide, and weighed as such.

<sup>1</sup> See also Fontès and Thivolle, *Bull. Soc. Chim. biol.*, 1922, 4, 614; 1923, 5, 325; *Bull. Soc. chim.*, 1923, [4], 33, 844; Feigl, *Chem. Zeit.*, 1923, 47, 561; Feigl and Neuber, *Zeitsch. anal. Chem.*, 1923, 62, 369; Vila, *Compt. rend.*, 1923, 177, 1219.

<sup>2</sup> A modified form of the Jones reductor is described by Wardlaw and Sylvester, *Trans. Chem. Soc.*, 1923, 123, 973.

<sup>3</sup> Knecht and Atack, *Analyt.*, 1911, 36, 98. For the determination of molybdenum and vanadium in a mixture of their acids, see Edgar, *loc. cit.*; Glassmann, *Ber.*, 1905, 38, 600.

<sup>4</sup> Jamieson, *J. Amer. Chem. Soc.*, 1917, 39, 246.

<sup>5</sup> Travers, *Compt. rend.*, 1917, 165, 362.

<sup>6</sup> Willard and Fenwick, *J. Amer. Chem. Soc.*, 1923, 45, 928.

<sup>7</sup> Malowan, *Chem. Zeit.*, 1918, 42, 410.

<sup>8</sup> Kollock and Smith, *J. Amer. Chem. Soc.*, 1901, 23, 669; Chilesotti and Rozzi, *Gazzetta*, 1905, 35, i, 228; Wherry and Smith, *J. Amer. Chem. Soc.*, 1907, 29, 806. For the separation of other metals from molybdenum by electrolysis, see McKay and Furman, *J. Amer. Chem. Soc.*, 1916, 38, 640; Treadwell, *Zeitsch. Elektrochem.*, 1913, 19, 219.

<sup>9</sup> Fischer and Weise, *Zeitsch. anal. Chem.*, 1912, 51, 537.

## CHAPTER VI.

### TUNGSTEN.

Symbol, W. Atomic weight, 184.0.

**Occurrence.**—Tungsten usually occurs in nature as tungstates of iron, manganese, and calcium. The most important mineral is *wolframite*, which consists essentially of an isomorphous mixture of iron and manganese tungstates,  $(\text{FeMn})\text{WO}_4$ . It is found in the Urals, Spain, Saxony, New England, Colorado, New South Wales, Malaya, and in Cumberland and Cornwall, usually in massive or platy aggregates of a black or brownish-black colour; sometimes in well-formed monoclinic crystals.<sup>1</sup> The ore possesses one very perfect cleavage<sup>2</sup> which causes it to split readily into thin flakes; it has density about 7.3 and hardness 5.5. It usually accompanies tin ores, from which it may be separated by electro-magnetic methods.<sup>3</sup> The proportions of iron and manganese present vary within wide limits, but usually  $\text{Fe} : \text{Mn} = 4 : 1$  or  $2 : 3$ . The most usual composition of wolframite is <sup>4</sup>  $\text{FeO} = 18.96$  per cent.;  $\text{MnO} = 4.67$  per cent.;  $\text{WO}_3 = 76.37$  per cent. Minerals containing more than 80 per cent.  $\text{MnWO}_4$  are known as *hübnerite*,<sup>5</sup> and such are found in Nevada and South Dakota. *Ferberite* was the name given to massive granular crystals of wolframite found with quartz in Southern Spain and believed to be pure ferrous tungstate,  $\text{FeWO}_4$ , a conclusion which was not borne out by analysis. However, specimens from South Dakota have been shown to contain no manganese. Ferrous tungstate also occurs as *reinite*, in Japan, in the form of tetragonal pyramids.

*Ferritungstite*,  $\text{Fe}_2\text{O}_3 \cdot \text{WO}_3 \cdot 6\text{H}_2\text{O}$ , occurs associated with quartz in the State of Washington. It is a brownish-yellow mineral which under the microscope is seen to consist of hexagonal plates.<sup>6</sup>

<sup>1</sup> des Cloizeaux, *Ann. Chim. Phys.*, 1870, 19, 168, states  $a : b : c = 0.8300 : 1 : 0.8678$ ;  $\beta = 89^\circ 21.6'$ .

<sup>2</sup> Rastall and Wilcockson, "Monograph on Mineral Resources with special reference to the British Empire," *Imperial Institute*, 1920.

<sup>3</sup> See Haüy, *J. des Mines*, 4, No. 19, 3; Rose, *Pogg. Annalen*, 1837, 40, 395; des Cloizeaux, *Compt. rend.*, 1869, 69, 868; D'Elhuyart, *J. des Mines*, 1794, 1, No. 4, 26; Vauquelin and Hecht, *ibid.*, 4, No. 19, 5; Bernouilli, *Pogg. Annalen*, 1860, 112, 607; Ebelmen, *Ann. Chim. Phys.*, 1843, [3], 8, 505; Schaffgotsch, *ibid.*, 1841, [3], 2, 532; Deville, *ibid.*, 1861, [3], 61, 344; Irving, *Trans. Amer. Inst. Mining Engin.*, 1901-02, 31, 683; Nicollardot, *Compt. rend.*, 1907, 144, 859; Finlayson, *Geol. Mag.*, 1910, [5], 7, 19; Granel, *Zeitsch. Kryst. Min.*, 1912, 50, 472; Wherry, *Proc. U.S. National Museum*, 1914, 47, 501.

<sup>4</sup> Dewey and Bromehead, "Special Report on Mineral Resources of Great Britain," vol. i., *Tungsten and Manganese Ores*, 1916, Mem., Geol. Survey.

<sup>5</sup> Hess and Schaller, *Bull. U.S. Geol. Survey*, No. 582, 1914.

<sup>6</sup> Schaller, *Amer. J. Sci.*, 1911, [4], 32, 161.

*Scheelite*, which is usually associated with crystalline rocks, is tetragonal calcium tungstate,  $\text{CaWO}_4$ , of density 6.00 and hardness 4 to 5. It is very widely distributed and usually, though not invariably, contains some molybdenum.<sup>1</sup> In Perak and Selangor fluorspar is usually found with it. It usually occurs in the massive form, generally of a yellow or pale brown colour, but sometimes reddish and possessing a curious waxy lustre.

*Tungstite*, or *tungsten ochre*, of which the colour varies from bright yellow to a greenish shade, occurs with wolframite in Cumberland and in Cornwall. It is essentially anhydrous tungsten trioxide,  $\text{WO}_3$ , though hydrated forms have been found. That described by Carnot<sup>2</sup> was said to correspond to the formula  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , and was called *meymacite*, while more recently<sup>3</sup> a tungstite, of density 5.52, apparently  $\text{WO}_3 \cdot \text{H}_2\text{O}$ , has been found in veins of gold quartz in British Columbia.

Other minerals containing tungsten are rare: *stolzite*,<sup>4</sup> of density 8.00, from Bohemia, Chili, and Massachusetts, is tetragonal lead tungstate,  $\text{PbWO}_4$ ; in the monoclinic form lead tungstate occurs as *raspite*; *chillagite*, a mixture of lead tungstate and lead molybdate, is found in Queensland; <sup>5</sup> *cuproscheelite* or *cuprotungstite*,  $(\text{CaCu})\text{WO}_4$ , is obtained from Chilian copper mines.<sup>6</sup> *Tungstenite*, a mineral analogous to molybdenite (see p. 111), occurs in Utah. It is essentially the sulphide  $\text{WS}_2$  (about 61 per cent.) and resembles graphite in appearance. It has density 7.4 and is soft enough to mark paper.<sup>7</sup>

**History.**—Until the middle of the eighteenth century both scheelite and wolframite were considered to be ores of tin; their real identity was first pointed out in 1781 by Scheele, who showed that the mineral now bearing his name contained lime combined with a new acid, which he named "tungstic acid." The metallic nature of the element was first demonstrated by Bergman.<sup>8</sup> Further researches were undertaken by D'Elhuyart,<sup>9</sup> Juan, José, and others.<sup>10</sup> The preparation of metallic tungsten, its industrial application (especially with regard to electrical glow lamps), and the study of its compounds have since been the subject of numerous researches.<sup>11</sup>

<sup>1</sup> See Berzelius, *Ann. Chim. Phys.*, 1821, [2], 17, 13; *ibid.*, 1816, [2], 3, 160; Rammelsberg, *Pogg. Annalen*, 1849, 77, 245; Lovisato, *Atti R. Accad. Lincei*, 1907, [5], 16, i., 632.

<sup>2</sup> Carnot, *Ann. Chim. Phys.*, 1874, [5], 3, 466; *Compt. rend.*, 1874, 79, 477; *Bull. Soc. chim.*, 1873, [2], 20, 488.

<sup>3</sup> Walker, *Amer. J. Sci.*, 1908, [4], 25, 305.

<sup>4</sup> Lévy, *Pogg. Annalen*, 1826, 8, 518; Brown, *Phil. Mag.*, 1847, [3], 31, 253.

<sup>5</sup> *Records of Geol. Survey, N.S.W.*, 1916, 9, 171.

<sup>6</sup> See also Tamm, *Chem. News*, 1873, 26, 13; *Bull. Soc. chim.*, 1873, [2], 19, 23; Mazade, *Compt. rend.*, 1851, 32, 685; Granel, *loc. cit.*

<sup>7</sup> Wells and Butler, *J. Washington Acad. Sci.*, 1917, 7, 596.

<sup>8</sup> Scheele, *J. Physique*, 1783, 22, 724; Bergman, *Acad. de Toulouse*, 1786, 2, 152; Berzelius, *Traité de Chimie*, 2nd ed., 2, 339.

<sup>9</sup> D'Elhuyart, *J. des Mines*, 1794, 1, No. 4, 26.

<sup>10</sup> See Roscoe and Schorlemmer, *A Treatise on Chemistry* (Macmillan & Co., London, 1907), 2, 1057; Cullen, *A Chemical Analysis of Wolfram, and Examination of a New Metal which enters into its Composition*, London, 1785.

<sup>11</sup> Some of the early work was accomplished by Ruprecht and Tondy, *Ann. Chim. Phys.*, 1791, [1], 8, 3; *J. Physique*, 1790, 37, 230; Vauquelin and Hecht, *J. des Mines*, 4, No. 19, 5; Allen and Aiken, *Encyclopédie Méthodique*, 1815, 6, 311; Buchholz, *Pogg. Annalen*, 1860, 111, 576; Berzelius, *Ann. Chim. Phys.*, 1825, [2], 17, 13; *Pogg. Annalen*, 1825, 4, 147; 1826, 8, 267; Wöhler, *ibid.*, 1823, [2], 29, 43; Malaguti, *ibid.*, 1835, [2], 60, 271; *Compt. rend.*, 1835, 1, 292; Forcher, *J. prakt. Chem.*, 1862, 86, 227; *Bull. Soc. chim.*, 1863, 5, 197; Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5; Roscoe, *Annalen*, 1872, 162, 349; *Chem. News*, 1873, 25, 61; *Bull. Soc. chim.*, 1872, 17, 209; Margueritte, *Ann. Chim.*

**Preparation.**—Scheelite is a preferable source of tungsten, the metal being more easily obtained from this than from other tungsten minerals.

In order to obtain pure tungstic anhydride,  $\text{WO}_3$ , or salts of the metal, from which tungsten may be prepared by suitable methods of reduction, the mineral concentrates are crushed and passed through a magnetic separator in order to remove tinstone and other impurities, and then oxidised by roasting in the air, care being taken that fusion does not occur; addition of an alkali solution then takes place, the tungsten being dissolved as alkali tungstate, while any iron and manganese remain as insoluble oxides. The necessary alkali may be added to the powdered mineral before roasting,<sup>1</sup> or the mineral may be decomposed by heating under pressure with caustic alkali<sup>2</sup> or by the use of an alkali silicate. Wöhler's method consists in fusing together wolframite with twice its weight of calcium chloride for one hour and extracting the melt with water. A solution of the chlorides of calcium, iron, and manganese is obtained, while the insoluble calcium tungstate,  $\text{CaWO}_4$ , on heating with concentrated hydrochloric acid, yields tungstic anhydride. Sodium hydrogen sulphate may be used for the decomposition of wolframite;<sup>3</sup> a mixture of soda and sodium nitrate,<sup>4</sup> or of the carbonates of sodium and potassium,<sup>5</sup> may also be employed.<sup>6</sup> Pure tungstic anhydride may then be obtained by solution in ammonia and reprecipitation by acids, or by reduction, conversion into the oxy-chloride, and treatment with acid.<sup>7</sup>

Metallic tungsten may be obtained by a number of methods, including processes similar to those employed in the case of chromium and molybdenum (see pp. 9 and 113).

1. *Reduction of Tungstic Anhydride with Carbon or Hydrogen.*—Reduction by carbon takes place at a red heat;<sup>8</sup> by employment of the electric furnace Moissan<sup>9</sup> reduced 800 grams of the trioxide with 80 grams of charcoal, using a current of 900 amperes at 50 volts for ten minutes, and obtaining a product containing 0.13 per cent. of carbon. Wolframite, though not reducible with zinc or magnesium, is reduced by carbon in the electric furnace, carbon being finally removed from the product by fusion with tungstic acid and calcium fluoride.<sup>10</sup>

*Phys.*, 1846, [3], 17, 475; *J. Pharm. Chim.*, 1845, 37, 222; Laurent, *Ann. Chim. Phys.*, 1847, [3], 21, 54; 1838, [2], 67, 219; *Annalen*, 1838, 28, 92; Persoz, *Ann. Chim. Phys.*, 1864, [4], 1, 93; Marignac, *ibid.*, 1863, [3], 69, 5; Lefort, *ibid.*, 1876, [5], 9, 93; 1878, [5], 15, 321; 1879, [5], 17, 470; Wöhler, *ibid.*, 1825, [2], 29, 50; 1850, [3], 29, 187; *Pogg. Annalen*, 1824, 2, 345; *Annalen*, 1850, 73, 190.

<sup>1</sup> Huntington, *German Patent*, 32360 (1884).

<sup>2</sup> Hempel, *German Patent*, 221062 (1907).

<sup>3</sup> Brandenburg and Weyland, *German Patent*, 149556 (1902); Clotten, *ibid.*, 141811 (1902).

<sup>4</sup> Franz, *J. prakt. Chem.*, 1871, [2], 4, 238; Hofmanns, *Ber.*, 1875, 9, 745.

<sup>5</sup> Derenbach, *Jahresber.*, 1893, p. 290.

<sup>6</sup> See also p. 202. A useful summary of methods used for the decomposition of tungsten minerals is given by Weber, *Die elektrischen Metallfadenglühlampen* (Leipzig, 1914), p. 100 *et seq.*; see also Mennicke, *Die Metallurgie des Wolframs* (1911).

<sup>7</sup> Ruff, *Zeitsch. angew. Chem.*, 1912, 25, 1889. See p. 202. For details of methods see Pennington and Smith, *Zeitsch. anorg. Chem.*, 1895, 8, 198; Filsinger, *Deutsche Industriezeitung*, 1878, p. 246; Friedheim and Meyer, *Zeitsch. anorg. Chem.*, 1892, 1, 76; Bernoulli, *Pogg. Annalen*, 1825, 3, 590.

<sup>8</sup> See Majert, *U.S. Patent*, 946551 (1910); Davis, *J. Ind. Eng. Chem.*, 1919, 11, 201.

<sup>9</sup> Moissan, *Compt. rend.*, 1893, 106, 1225; similarly (from wolframite) Siemens and Huntington, *Ann. Chim. Phys.*, 1883, [5], 30, 465; Defacqz, *Compt. rend.*, 1896, 123, 1288.

<sup>10</sup> Weiss, Martin, and Stimmelmayer, *Zeitsch. anorg. Chem.*, 1910, 65, 279.

Probably the best method available for the preparation of pure tungsten is the reduction in a porcelain tube of purified tungsten trioxide contained in nickel boats by means of pure dry electrolytic hydrogen (the desiccation being effected by phosphoric anhydride) at  $1100^{\circ}$  to  $1150^{\circ}$  C.<sup>1</sup>

2. *Reduction of Tungstic Anhydride with Metals.*—Tungsten for the manufacture of metallic filament electric glow lamps was formerly obtained by a modification of Delépine's process, consisting of reduction of the trioxide by heating with powdered zinc, and removal of the excess of zinc and zinc oxide by treatment with acids.<sup>2</sup> If Goldschmidt's aluminothermic method of reduction is applied, the reaction is very violent and an alloy containing 2.6 per cent. aluminium is obtained. The presence of this impurity is undesirable for filament manufacture. It is preferable to use a deficiency of aluminium and to treat the product with hydrochloric acid.<sup>3</sup> Metallic calcium may also be used for reduction.<sup>4</sup>

3. *Reduction of tungsten chloride*, either by heating alone at  $1000^{\circ}$  to  $1500^{\circ}$  C. when the compound dissociates, leaving a residue of pure tungsten,<sup>5</sup> or by means of hydrogen<sup>6</sup> or sodium.<sup>7</sup> The reduction of the chloride or rather oxychloride by means of carbon and hydrogen is applied to the manufacture of filaments for tungsten glow lamps (p. 185) in connection with which the details of the process are presently described.

4. *Electrolytic Methods.*—The metal is obtained in the amorphous condition by the electrolysis of fused sodium tungstate,<sup>8</sup> and in globules containing 96 per cent. of tungsten when a solution of the trioxide in cryolite is electrolysed.<sup>9</sup> A good deposit of very pure tungsten may be obtained by electrolysis of a solution of tungstic acid in a fused mixture of sodium and potassium chlorides<sup>10</sup> if less than 1 part of the acid to 2 parts of fused chloride is present. A solution of the hexachloride in certain organic liquids, e.g. acetone, when submitted to electrolysis under suitable conditions, yields metallic tungsten.<sup>11</sup>

<sup>1</sup> Ruff, *Zeitsch. angew. Chem.*, 1912, 25, 1889; Davis, *loc. cit.*; Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5; Roscoe, *Annalen*, 1872, 162, 349; *Chem. News*, 1873, 25, 61; *Bull. Soc. chim.*, 1872, 17, 209. Several modifications of the original process have been described: see Ruhstrat, *German Patents*, 215347 (1907); 220176 (1909); *British Patent*, 24437 (1909); Badische Anilin- und Soda-fabrik, *D.R.-Patentanmeldung*, 1911, B. 65694, Kl. 40a; Schwarzkopf, *ibid.*, 1911, Sch. 39510, Kl. 21f.

<sup>2</sup> Delépine, *Compt. rend.*, 1900, 131, 184; Hollefreund, *German Patent*, 221899 (1906).

<sup>3</sup> Weiss, *Zeitsch. anorg. Chem.*, 1910, 65, 279; Stavenhagen, *Ber.*, 1899, 32, 1513, 3064; 1902, 35, 909; *Bull. Soc. chim.*, 1902, [3], 28, 518; Voigtländer, *D.R.-Patentanmeldung*, 1913, V. 10743, Kl. 40a; Goldschmidt and Valentin, *Zeitsch. Elektrochem.*, 1898, 4, 494; *J. Soc. Chem. Ind.*, 1898, 17, 649; Ruhstrat, *German Patent*, 217781 (1908).

<sup>4</sup> Wedekind, *D.R.-Patentanmeldung*, 1909, Kl. 40, K. 42377.

<sup>5</sup> Pring and Fielding, *Trans. Chem. Soc.*, 1909, 95, 1502.

<sup>6</sup> Wöhler and Uslar, *Annalen*, 1855, 94, 255.

<sup>7</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5.

<sup>8</sup> Zettnow, *Pogg. Annalen*, 1867, 130, 16; *Bull. Soc. chim.*, 1867, [2], 8, 37, 174. See also Hallopeau, *Compt. rend.*, 1898, 127, 755, and Stavenhagen, *Ber.*, 1899, 32, 3064, on the electrolysis of fused lithium paratungstate.

<sup>9</sup> L. and H. H. Kahlenberg, *J. Amer. Electrochem. Soc.*, 1924, 46, 51.

<sup>11</sup> Leiser, *Zeitsch. Elektrochem.*, 1907, 13, 690; Wedekind, *D.R.-Patentanmeldung*, 1909, Kl. 40, K. 42377; Wolframlampen Akt.-Ges., *German Patents*, 237014, 231657 (1910); Fischer and others, *Zeitsch. anorg. Chem.*, 1913, 81, 170; Rosenheim and Bernhardt-Grisson, *VIIth Intern. Congr. Appl. Chem.*, 1911, Section X, p. 120; Neumann and Richter, *Zeitsch. Elektrochem.*, 1924, 30, 474.

5. *Other methods*, for a detailed description of which the literature should be consulted, have been employed.<sup>1</sup>

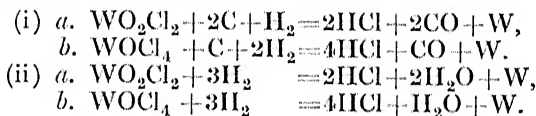
**Tungsten Filaments** for electric glow lamps may be made by one of a number of distinct processes, viz. :

1. Mechanical drawing of rods or wires of the pure metal. Finely divided tungsten pressed into the form of wire may be drawn slowly through an orifice surrounded by a small coil maintained at a temperature of 2000° to 2200° C.<sup>2</sup> If the rate at which the wire travels is properly regulated, the tungsten forms a single homogeneous elongated crystal, the rate of growth of which equals the forward movement of the wire. The mean diameter of the particles is about 10<sup>-5</sup> cm., and X-ray examination shows the crystalline form to be cubic.<sup>3</sup>

2. Compression of a paste of tungsten powder with a suitable organic compound, carbonisation of the crude filament, and finally sintering and shaping the product. This is probably the chief method now in application.

3. Compression of colloidal tungsten without the use of a binding material.<sup>4</sup> The requisite colloidal solution is obtained by making an electric arc between tungsten electrodes under water,<sup>5</sup> by heating the powdered element alternately in acids and alkalis,<sup>6</sup> or by the reduction of pure tungsten trioxide by means of potassium cyanide, this method being dependent upon the formation of an oxynitride.<sup>7</sup>

4. By a method of substitution or exchange, consisting of the introduction of a glowing metal- or carbon-filament into an atmosphere of tungsten oxychloride vapour and excess of hydrogen. Metallic tungsten is deposited upon the filament which thus consists of a core of carbon (or metal) enclosed in a tube of tungsten.<sup>8</sup> According to the conditions, the carbon may be partially or completely replaced by the tungsten, and homogeneous filaments are readily obtained. The reactions which take place may be symbolised as follows :—



A number of other methods and improvements upon the above have

<sup>1</sup> Westinghouse Metal Filament Lamp Co., *German Patent*, 199107 (1906); Regina-Bogenlampenfabrik, *German Patent*, 228286 (1908); Wolframlampen Akt.-Ges., *German Patent*, 239877 (1910); Schilling, *German Patent*, 249314 (1908); Electric Furnaces and Smelters, Ltd., *German Patent*, 247993 (1911); Johnson, *German Patent*, 246182 (1910). Some account of these and the foregoing methods is to be found in Weber, *Die elektrischen Metallfadengühlampen*, Leipzig, 1914. Wöhler's method consists in heating the compound  $\text{W}_3\text{N}_6\text{H}_4$  (see p. 249).

<sup>2</sup> Gross, *Jahrb. Radioaktiv. Elektronik.*, 1918, **15**, 270.

<sup>3</sup> Debye, *Physikal. Zeitsch.*, 1917, **18**, 483.

<sup>4</sup> Kužel, *German Patent*, 194348 (1905).

<sup>5</sup> See Billitzer, *Zeitsch. angew. Chem.*, 1898, **11**, 951.

<sup>6</sup> Schulz, *J. prakt. Chem.*, 1885, **32**, 399.

<sup>7</sup> Desi, *J. Amer. Chem. Soc.*, 1897, **19**, 239; Kužel, *German Patent*, 199962 (1907). For further information see Julius Pintsch Akt.-Ges., *German Patents*, 205581, 206911 (1905); 216785 (1906); Pacz, *German Patents*, 245190 (1909); 249733 (1910); Kužel, *German Patent*, 208599 (1908); Planchon, *German Patents*, 220981, 220982 (1908); Siemens and Halske, *German Patents*, 194468 (1906); 201462 (1907); 200939 (1907).

<sup>8</sup> Just and Hanaman, *German Patent*, 154262 (1903); *Electrochem. and Metall. Ind.*, 1909, **7**, 24; Wolframlampen Akt.-Ges., *German Patents*, 184379 (1905); 185906 (1906); 182766 (1904); 193221 (1906).



been worked out. Reference to the patent literature upon the subject is made below.<sup>1</sup>

The use of tungsten for glow lamp filaments depends on its high melting-point and comparative non-volatility at high temperatures. The tungsten powder used in the above preparations is usually obtained by reduction of tungsten trioxide to which has been added a little thorium nitrate, so that the filament generally contains thorium oxide to the extent of from 0.7 to 1.0 per cent. In the absence of thoria, rapid crystal growth occurs on burning the filament, which generally has a fibrous structure, and the crystal boundaries extending across the filament cause weakness and liability to fracture. The presence of thoria, which segregates at the boundaries between the crystal grains, greatly reduces the tendency to crystal growth and so increases the durability of the filament. It has been shown that during the burning reduction of the oxide to thorium takes place.<sup>2</sup> If the filament consists of a single elongated crystal, as when prepared by the first process described above, the possibility of such crystal growth is eliminated.<sup>3</sup> In the ordinary evacuated tungsten lamp a temperature of about 2130° C. is obtained with safety, but if a higher temperature is reached, the tungsten begins to volatilise and condenses as a black deposit on the glass, which greatly reduces the efficiency of the lamp. It has been found that the dimming effect of this deposit may be overcome by coating the filament, previous to burning, with a layer of certain salts; <sup>4</sup> for example, sodium chloride, sodium phosphate, potassium cyanide, or calcium fluoride. On passing the current the salt sublimes and condenses in a non-crystalline condition on the wall of the lamp, the tungsten sublimate is decolorised and its power of light absorption diminished. The effect does not appear to be due to any chemical action, but to the formation of solid solutions of tungsten in salt which have a considerably lower light absorption than the coherent metal films.<sup>5</sup> The volatilisation of the tungsten may also be greatly reduced by filling the lamp with an inert gas such as nitrogen or argon <sup>6</sup> under diminished pressure, usually about half an atmosphere. Higher temperatures may safely be reached with such lamps, and powerful illumination is obtained by this means.<sup>7</sup>

**Physical Properties.**—Metallic tungsten, according to its method

<sup>1</sup> Westinghouse Metal Filament Lamp Co., Ltd., *D.R.-Patentanmeldung*, 1908, Kl. 21f, W. 27972; Wolframlampen Akt.-Ges., *German Patents*, 185585 (1905); 231492 (1906); Heinrich, *German Patent*, 214493 (1909); Lux, *German Patents*, 188509, 216903, 200938, 210325, 193920, 212962 (1905); 194894, 212104 (1906); British Thomson-Houston Co., *British Patents*, 11409 (1906); 25557 (1908); 5821 (1909); Goossens, Pope & Co., *German Patent*, 207163 (1907); Siemens and Halske Akt.-Ges., *German Patent*, 201283 (1906); Kitsée, *German Patent*, 236710 (1910); Müller, *Helios, Zeitsch. für Elektrotech.*, 1913, 19, No. 40, 505; Bainville, *L'Electricien*, 1912, No. 1123, 6. A summary of the processes referred to will be found in Weber, *Die elektrischen Metallfadenglühlampen*, Leipzig, 1914, which contains a useful summary of the industry and of the metallurgy of tungsten.

<sup>2</sup> Langmuir, *British Patent*, 148132 (1922); Smithells, *Trans. Chem. Soc.*, 1922, 121, 2236; *Trans. Faraday Soc.*, 1922, 17, 485; *J. Inst. Metals*, 1922, 27, 107.

<sup>3</sup> On the properties of such filaments see van Arkel, *Physica*, 1923, 3, 76; Research Staff of General Electric Co., Ltd., *Phil. Mag.*, 1924, [6], 48, 800.

<sup>4</sup> Hamburger, Holst, Lely, and Oosterhuis, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1078.

<sup>5</sup> See Svedberg, *The Formation of Colloids* (Churchill, 1921), p. 18.

<sup>6</sup> Langmuir, and Langmuir and Orange, *Met. Chem. Eng.*, 1913, 11, 613. See also Langmuir, *J. Amer. Chem. Soc.*, 1915, 37, 1139.

<sup>7</sup> For a description of a special type of tungsten lamp which can be used for microscopic work and polarimetry, see M'Dermott, *J. Amer. Chem. Soc.*, 1914, 36, 454.

of preparation, is silver white, resembling highly polished platinum, or is crystalline in structure, or is a grey powder.<sup>1</sup> When heated in air, coloured films are formed as in the case of steel.<sup>2</sup> It has a hardness of 6.5 to 7.5 and a density at 20° C. of 18.72.<sup>3</sup> It melts at 3267° ± 30° C.<sup>4</sup> and boils at about 5000° Abs.<sup>5</sup> Its heat of evaporation is very high, being about 218000—1.8 T gram calories per gram atom. The vapour pressure of tungsten at its melting-point is 0.080 mm.<sup>6</sup> Moissan<sup>7</sup> found that tungsten, like molybdenum and uranium, was very refractory, but might be distilled in the electric furnace. Its specific heat at ordinary temperatures is 0.0358.<sup>8</sup> At high temperatures the atomic heat is almost linear between 1200° C. and 2400° C., the values at these temperatures being respectively 6.25 and 7.35 calories per gram atom degree.<sup>9</sup> The coefficients of linear expansion increase regularly with temperature; from —100° C. to 0° C. the average coefficient is  $4.2 \times 10^{-6}$  per degree centigrade, whilst from 0° C. to 500° C. the average value is  $4.6 \times 10^{-6}$  per degree centigrade.<sup>10</sup> The compressibility of tungsten, which at 20° C. is  $11 \times 0.28 \times 10^{-6}$  per megabar, is the smallest of any hitherto studied. Tungsten is non-magnetic.<sup>12</sup> Its magnetic susceptibility between 18° and 1100° C. is +0.33.<sup>13</sup> Measurements of its electrical resistance at 1000° to 2000° C. have been made.<sup>14</sup> The emission of electrons from heated tungsten has been observed,<sup>15</sup> and also, though only at temperatures above 2500° C., of slow-moving positive ions.<sup>16</sup> By charging a condenser to 30,000 to 40,000 volts and rapidly discharging it through a short tungsten wire of 0.035 mm. diameter in a vacuum,<sup>17</sup> tungsten

<sup>1</sup> Wartenberg, *Ber.*, 1907, 40, 3287; Ruff, *Zeitsch. angew. Chem.*, 1912, 25, 1889; Hallopeau, *Compt. rend.*, 1898, 127, 755; Férée, *Bull. Soc. chim.*, 1898, [3], 19, 123, describes the pyrophoric form.

<sup>2</sup> Weiss, *Zeitsch. anorg. Chem.*, 1910, 65, 279.

<sup>3</sup> Weiss, *loc. cit.* Wartenberg, *Ber.*, 1907, 40, 3289, states massive tungsten has a density of 17.6–18.3, and the powder 19.0–19.2. Cf. Ref. 10 below. See also Pennington and Smith, *Zeitsch. anorg. Chem.*, 1895, 8, 198; Moissan, *Compt. rend.*, 1896, 123, 13; Hallopeau, *loc. cit.* Determinations also by Allen and Aiken, Buchholz, D'Elhuyart, Bernoulli, Zettnow, Roscoe, Uslar, Riche, Delépine.

<sup>4</sup> Langmuir, *Chem. Zentr.*, 1916, i, 205; *Phys. Review*, 1915, 6, 138; *J. Franklin Inst.*, 1915, 180, 490. Cf. Worthing, *Zeitsch. Physik*, 1924, 22, 9. See also *J. Amer. Chem. Soc.*, 1913, 35, 931. Pirani and Meyer, *Ber. Deut. physikal. Ges.*, 1912, 14, 426, gives 3100° ± 60° C. Wartenberg, *loc. cit.*, gives 2800°–2850° C. See also Ruff and Goecke, *Zeitsch. angew. Chem.*, 1911, 24, 1459. The Bureau of Standards, *Circular No. 7*, 1910, gives the value 3000° C.

<sup>5</sup> Calculated value due to Langmuir, *J. Amer. Chem. Soc.*, 1913, 35, 931. The value 3700° C. is given by Fink, *Trans. Amer. Electrochem. Soc.*, 1912, 22, 490.

<sup>6</sup> Langmuir, *loc. cit.*

<sup>7</sup> Moissan, *Compt. rend.*, 1906, 142, 425.

<sup>8</sup> Weiss, *loc. cit.* At 800°–1500° C. Corbino, *Atti R. Accad. Lincei*, 1912, [5], 21, i, 188, 346, found the value 0.0424. Compare Worthing, *Bull. Nela Res. Lab.*, 1922, i, 349. Regnault (*Ann. Chim. Phys.*, 1840, [2], 73, 48; 1861, [3], 63, 23; *Bull. Soc. chim.*, 1862, 4, 83) found the value 0.03342. See also Grodspeed and Smith, *Zeitsch. anorg. Chem.*, 1895, 8, 207; Defaegh and Guichard, *Ann. Chim. Phys.*, 1901, [7], 24, 139; Nordmeyer and Bernoulli, *Verh. Deut. Phys. Ges.*, 1907, 9, 125.

<sup>9</sup> Worthing, *J. Franklin Inst.*, 1918, 185, 707.

<sup>10</sup> Hildert and Sweeney, *Thermal Expansion of Tungsten*, Scientific Paper of the Bureau of Standards, No. 515, 1925. The metal used contained 99.98 per cent. tungsten, and had a density of 19.211. The paper contains a useful summary of expansion data by previous observers.

<sup>12</sup> Weiss, *loc. cit.*

<sup>11</sup> Richards and Bartlett, *J. Amer. Chem. Soc.*, 1915, 37, 470.

<sup>13</sup> Honda, *Ann. Physik*, 1910, [4], 32, 1027.

<sup>14</sup> Pirani, *Physikal. Zeitsch.*, 1912, 13, 753.

<sup>15</sup> Richardson, *Phil. Mag.*, 1913, [6], 26, 345; *Physikal. Zeitsch.*, 1913, 14, 793; Langmuir, *ibid.*, 1914, 15, 516; Dushman, Rowe, and Kidner, *Phys. Review*, 1923, 21, 207.

<sup>16</sup> Jenkins, *Phil. Mag.*, 1924, [6], 47, 1025.

<sup>17</sup> Wendt and Irion, *J. Amer. Chem. Soc.*, 1922, 44, 1887. See also Anderson, *Astro-physical Journal*, 1920, 51, 37.

wire is completely dissipated, no solid residue or smoke remaining. Momentary temperatures of about  $20,000^{\circ}$  C. are obtained in this way, and it was at first thought that some of the tungsten atoms might be disintegrated in this manner, evolving helium nuclei. Apparently, however, even this violent disturbance is unable to disrupt the atomic system of the element.<sup>1</sup>

The electrical potential of tungsten in solutions of different acids, bases, and salts has been measured<sup>2</sup> against certain standard electrodes at  $25^{\circ}$  C. The tungsten does not behave as an insoluble electrode, but sends ions into the solutions. Under certain specified conditions—for example, with high-current densities (2 amperes per square decimetre) in aqueous alkalis, but with low-current densities in aqueous solutions of acids and salts—the tungsten anode becomes passive. The passivity appears to be due to adherent films of hydrated oxides. The electrochemical equivalent of tungsten has been found to be 0.3173 mg. per coulomb,<sup>2</sup> which is in close agreement with the theoretical value.

**Spectrum.**<sup>3</sup>—Leonard (*loc. cit.*)<sup>4</sup> examined the spark spectrum of solutions of sodium tungstate, finding the most *persistent* lines in the more refrangible part of the spectrum, the results being as follows:—

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
4680.8	6 $\phi$	2980.0	2 $\phi$	2679.8	4 $\chi$
4660.0	6 $\phi$	2977.3	2 $\phi$	2664.4	4 $\phi$
4610.1	2 $\sigma$	2947.1	3 $\chi$	2658.1	7 $\chi$
4802.3	6 $\phi$	2944.5	3 $\chi$	2656.6	2 $\chi$
4294.8	8 $\chi$	2935.1	3 $\phi$	2653.6	3 $\chi$
4269.5	6 $\phi$	2923.2	1 $\sigma$	2647.8	4 $\chi$
4074.5	6 $\chi$	2896.15	2 $\phi$	2632.9	2 $\phi$
4070.0	6 $\chi$	2879.5	2 $\psi$	2620.2	4 $\phi$
4008.9	8 $\chi$	2866.4	2 $\phi$	2615.5	4 $\chi$
3780.9	4 $\phi$	2848.2	1 $\phi$	2608.5	1 $\chi$
3768.6	4 $\phi$	2831.5	2 $\psi$	2603.1	4 $\chi$
3750.9	2 $\phi$	2774.6	3 $\phi$	2581.2	4 $\phi$
3617.7	6 $\phi$	2764.4	4 $\chi$	2572.3	4 $\psi$
3215.7	4 $\chi$	2729.69	4 $\phi$	2563.2	4 $\psi$
3051.4	4 $\chi$	2724.2	4 $\chi$	2555.1	4 $\psi$
3049.9	3 $\chi$	2709.7	4 $\phi$	2551.5	3 $\phi$
3024.5	4 $\phi$	2702.2	4 $\phi$	2531.1	3 $\chi$
3017.6	2 $\phi$	2697.8	4 $\chi$	2522.1	4 $\sigma$
3014.3	1 $\sigma$	2694.5	2 $\phi$		

<sup>1</sup> Briscoe, Robinson, and Stephenson, *Trans. Chem. Soc.*, 1925, 127, 240. Cf. Smith, *Proc. Nat. Acad. Science*, 1924, 10, 4; Harkins and Allison, *J. Amer. Chem. Soc.*, 1924, 46, 814.

<sup>2</sup> Koerner, *Trans. Amer. Electrochem. Soc.*, 1917, 31, 221.

<sup>3</sup> References to the literature on the spectrum of tungsten are as follows: Barnes, *Phil. Mag.*, 1915, [6], 30, 368; Jack, *Proc. Roy. Soc. Edin.*, 1909, 29, 75; Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 270; Hasselberg, *K. Svenska Vet.-Akad. Handl.*, 1904, 38, No. 5, 1; Exner and Haschek, *Die Spectren der Elemente bei normalem Druck*, Leipzig, 1911; Humphreys, *Smithsonian Misc. Collection*, 1902, p. 363; *Astrophys. J.*, 1897, 6, 169, 232; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1895, 104; 1896, 105; 1897, 106; Lookyer, *Phil. Trans.*, 1881, 173, 561; Thalen, *Nov. acta Reg. Sci. Upsala*, 1868, [3], 6; *Ann. Chim. Phys.*, 1869, [2], 18, 242.

<sup>4</sup> See p. 14 for a general description of the method and for list of abbreviations used.

Exner and Haschek (*loc. cit.*) record the following lines as being the most *intense* :—<sup>1</sup>

Arc Spectrum.		Spark Spectrum.		Arc Spectrum.		Spark Spectrum.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
4008.91	10 *	2397.18	10	5224.85	20	4008.93	10
4294.77	10 *	2702.22	10	5492.51	15	4294.81	10
4484.37	10	3077.61	10	5514.88	20 *	5006.33	10
4843.99	10 *	3376.30	10	5648.57	10	5053.50	15
5006.32	10	3572.65	10	5735.31	15 *	5071.94	10
5015.49	10 *	3592.59	10	5805.09	10	5224.89	20
5053.48	15 *	3613.98	10			5492.57	15
		3641.57	10			5514.91	20 *
		3736.39	10			5648.61	10

In the arc spectrum of tungsten the wave-lengths of 478 lines up to 9159 Å have been measured by Kiess and Meggers.<sup>2</sup>

**Chemical Properties.**—Tungsten is not oxidised appreciably in air below red heat, nor is it at any known temperature, unless in the vaporous state, attacked by nitrogen.<sup>3</sup> Halides are formed directly, the fluoride at ordinary temperatures, the iodide at a bright red heat, and the others intermediately. On heating in the electric furnace with carbon, boron, or silicon, combination takes place.<sup>4</sup> Neither sulphur nor phosphorus has any action upon the metal. At a red heat it decomposes water ; <sup>5</sup> it is not attacked by a solution of caustic potash, but by fused alkalis it is dissolved,<sup>6</sup> though more rapidly by a fused mixture of potassium carbonate and nitrate.<sup>7</sup> Oxidation attended by incandescence takes place on heating the powdered metal with certain oxidising agents such as lead dioxide and potassium chlorate.

Tungsten, like molybdenum, is very resistant to the action of acids ; this is largely due to the formation of a protective coating of oxide. Neither aqua regia nor hydrofluoric acid dissolves the metal to any appreciable extent : the best solvent for the fused metal is a mixture of concentrated nitric and hydrofluoric acids.<sup>8</sup>

**Atomic Weight.**—Like chromium and molybdenum, tungsten may in its compounds be di-, tri-, or hexa-valent ; from a consideration of its specific heat, the isomorphism of its compounds, its position in the

<sup>1</sup> See p. 13 for explanation of abbreviations.

<sup>2</sup> Kiess and Meggers, *Bureau Standards Bulletin*, 1920, 16, 51. See also Belke, *Zeitsch. wiss. Photochem.*, 1917, 17, 132, 145. The X-ray spectrum of tungsten has been investigated by Barnes, *Phil. Mag.*, 1915, [6], 30, 368; Ledoux-Lebard and Dauvillier, *Compt. rend.*, 1917, 164, 687; Siegbahn, *Phil. Mag.*, 1919, [6], 38, 639. Cf. de Broglie, *Compt. rend.*, 1919, 169, 962; 1920, 170, 1053; Duane and Shimizu, *Phys. Review*, 1919, 13, 306; Duane and Patterson, *ibid.*, 1920, 16, 526; *Proc. Nat. Acad. Sci.*, 1920, 6, 509; Duane and Stenström, *ibid.*, 1920, 6, 477; Smekal, *Zeitsch. Physik*, 1921, 5, 91; Dauvillier, *Compt. rend.*, 1921, 173, 647; Crofutt, *Proc. Iowa Acad. Sci.*, 1921, 28, 117; *Phys. Review*, 1924, 24, 9; Yoshida and Tanaka, *Mem. Coll. Sci. Kyoto*, 1922, 5, 173; Rogers, *Proc. Camb. Phil. Soc.*, 1923, 21, 430; Cork, *Phys. Review*, 1923, [2], 21, 326.

<sup>3</sup> Ruff, *Zeitsch. angew. Chem.*, 1912, 25, 1889; Langmuir, *J. Amer. Chem. Soc.*, 1913, 35, 105, 931; Sieverts and Bergner, *Ber.*, 1911, 44, 2394.

<sup>4</sup> Moissan, *Ann. Chim. Phys.*, 1896, [7], 8, 570; *Compt. rend.*, 1893, 116, 1225; 1896, 123, 13.

<sup>5</sup> See Wöhler and Prager, *Zeitsch. Elektrochem.*, 1917, 23, 199.

<sup>6</sup> Ruder, *J. Amer. Chem. Soc.*, 1912, 34, 387.

<sup>7</sup> Moissan, *loc. cit.*

<sup>8</sup> Ruder, *loc. cit.*; Weiss, *Zeitsch. anorg. Chem.*, 1910, 65, 279.

periodic classification, the molecular weights of a number of its compounds and other data (see Vol. I., p. 233), its atomic weight is known to be six times its equivalent in tungstic anhydride, or three times its equivalent in the tungstic salts.

The determinations of the atomic weight of tungsten which have been published are appended: <sup>1</sup>

Date.	Investigator.	Ratio Measured.	Result.
1826	Berzelius . .	$\text{WO}_3 : \text{W}$	189.324
1836	Malaguti . .	$\text{WO}_3 : \text{W}_2\text{O}_5$	too high
1850	Schneider . .	$\text{WO}_3 : \text{W}$	184.108
1851	Marchand . .	$\text{WO}_3 : \text{W}$	184.114
1851	von Borch . .	$\text{WO}_3 : \text{W}$	183.806
1857	Riche . .	$\text{WO}_3 : \text{W}$	no value
1860	Dumas . .	$\text{WO}_3 : \text{W}$	184.019
1860	Bernoulli . .	$\text{WO}_3 : \text{W}$	185.918
1861	Scheibler . .	$\text{BaO} \cdot 4\text{WO}_3 \cdot 9\text{H}_2\text{O} : 9\text{H}_2\text{O}$	184.0
1864	Persoz . .	$\text{WO}_3 : \text{W}$	184.041
1867	Zettnow . .	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} : \text{FeWO}_4$	183.6
		$\text{Ag}_2\text{WO}_4 : 2\text{AgCl}$	
		$\text{WO}_3 : \text{W}$	
1872	Roscoe . .	$\text{WCl}_6 : \text{WO}_3$	183.482
		..	184.10
1883	Meyer and Seubert	$\text{WO}_3 : \text{W}$	183.6
1886	Waddell . .	..	184.332
1891	Ostwald . .	..	184.0
1891	Clarke . .	..	183.5
1894	Smith and Desi .	$\text{WO}_3 : 3\text{H}_2\text{O}$	184.65
1895	Pennington and Smith.	$\text{W} : \text{WO}_3$	184.92
1896	Schneider . .	$\text{W} : \text{WO}_3$	184.007
1896	Shinn . .	$\text{W} : \text{WO}_3$	184.908
1897	Hardin . .	$\text{WO}_3 : \text{W}$	184.105
1899	Thomas . .	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} : 2\text{H}_2\text{O}$	183.9
1901	Taylor . .	$\text{WO}_3 : \text{CO}_2$	183.47
1904	Smith and Exner	$\text{W} : \text{WO}_3$	184.075
		$\text{WCl}_6 : \text{WO}_3$	184.10
		$\text{WO}_3 : \text{CO}_2$	183.55

Berzelius, *Pogg. Annalen*, 1826, 8, 1; Malaguti, *J. prakt. Chem.*, 1836, 8, 179; Schneider, *ibid.*, 1850, 50, 152; 1896, [2], 53, 288; Marchand, *Annalen*, 1851, 77, 261; von Borch, *J. prakt. Chem.*, 1851, 54, 254; Riche, *ibid.*, 1857, 69, 10; Dumas, *Annalen*, 1860, 113, 23; Bernoulli, *Pogg. Annalen*, 1860, 111, 573; Scheibler, *J. prakt. Chem.*, 1861, 83, 324; Persoz, *Zeitsch. anal. Chem.*, 1864, 3, 260; Zettnow, *Pogg. Annalen*, 1867, 130, 30; Roscoe, *Annalen*, 1872, 162, 368; Meyer and Seubert, *Die Atomgewichte der Elemente* (Leipzig, 1883); *Pharmaceutische Rundschau von Hoffmann* (New York, 1891); Waddell, *Amer. Chem. J.*, 1886, 8, 280; Ostwald, *Lehrbuch der allgemeinen Chemie*, 1891, 1, 30-125; Clarke, *Pharmaceutische Rundschau von Hoffmann* (New York, 1891); Smith and Desi, *Zeitsch. anorg. Chem.*, 1895, 8, 205; Pennington and Smith, *ibid.*, 1895, 8, 202; Shinn, *Thesis* (University of Pennsylvania, 1896); Hardin, *J. Amer. Chem. Soc.*, 1897, 19, 657; 1899, 21, 1017; Thomas, *ibid.*, 1899, 21, 373; Taylor, *Thesis* (University of Pennsylvania, 1901); Smith and Exner, *Proc. Amer. Phil. Soc.*, 1904, 43, 123; *J. Amer. Chem. Soc.*, 1904, 26, 1082; *Chem. News*, 1904, 90, 37, 49, 66.

<sup>1</sup> See Moissan, *Traité de Chimie*, 1905, 4, 764; Clarke, "A Recalculation of the Atomic Weights," *Smithsonian Misc. Coll.*, 3rd ed., 1910, p. 359. The values given are recalculated on the basis of the fundamental atomic weights, see p. 17.

As regards the values for the atomic weight of tungsten obtained by determination of the ratio  $W : WO_3$ , that obtained by Smith and Exner (*loc. cit.*) is by far the most trustworthy. Clarke <sup>1</sup> finds that their value is almost identical with his weighted mean of twelve other reasonably reliable determinations based upon the same method, excluding that of Pennington and Smith (*loc. cit.*). The mean atomic weight deduced from the nine different ratios that have been measured thus yields a value of  $184.575 \pm 0.026$ , but Clarke (*loc. cit.*) considers that the most reliable value is the mean of Smith and Exner's determinations of the ratios  $WO_3 : W$  and  $WCl_6 : WO_3$ , *i.e.*  $W = 184.092 \pm 0.046$ , a conclusion which is supported by the fact that this combination of the two ratios of Smith and Exner gives a good value (35.454) for the atomic weight of chlorine. The International Committee for 1925 give the value  $W = 184.0$ .

**Uses.**—In addition to its employment for lamp filaments, tungsten is now used instead of platinum for much electrical work. Its hardness, good heat conductivity, and high melting-point renders it suitable for contacts or arcing points subject to great temperature changes, and for wiring electric tube furnaces.<sup>2</sup> The addition of the metal to steels gives increased hardness and tensile strength, so that tungsten steels are much used for the manufacture of high-speed tools. On account of its low volatility the metal is also used for the targets of X-ray tubes.

**Alloys.**—Tungsten enters into the composition of many useful alloys. Aluminium and tungsten readily unite. Several alloys, the percentage compositions of which correspond to the possible formulae  $Al_7W$ ,  $Al_5W$ ,  $Al_4W$ ,  $Al_3W$ , and  $AlW_2$ , have been described. The alloy corresponding to the formula  $Al_5W$  forms large, thin, monoclinic crystals and is readily attacked by aqua regia, whereas that corresponding to the formula  $Al_7W$  forms hexagonal crystals which are insoluble in aqua regia and only sparingly attacked by a fused mixture of alkali carbonate and nitrate.<sup>3</sup>

The preparation of alloys with *chromium* in all proportions has been described,<sup>4</sup> together with that of alloys with *chromium* and *iron* and with *chromium*, *copper*, and *iron*.<sup>5</sup> An alloy resembling stellite, but containing 20 per cent. tungsten, 15 per cent. chromium, and 65 per cent. cobalt, is very hard and is used for cutting tools and for surgical instruments,<sup>6</sup> since it is unaffected by organic acids or ordinary antiseptics. A similar alloy, also used for the latter purpose, is known as *amaloy* and contains tungsten, chromium, and nickel. Certain alloys with copper and nickel are highly resistant to concentrated mineral acids<sup>7</sup> and are used as substitutes for platinum.

<sup>1</sup> Clarke, "A Recalculation of the Atomic Weights," *Smithsonian Misc. Coll.*, 3rd ed., 1910, p. 367.

<sup>2</sup> Compton (*J. Optical Soc. Amer.*, 1922, 6, 910) describes a furnace consisting of a tube of sheet tungsten wound with tungsten wire.

<sup>3</sup> Campbell and Mathews, *J. Amer. Chem. Soc.*, 1902, 24, 253; Guillet, *Compt. rend.*, 1901, 132, 1112; *Génie civil*, 1902, 41, 363, 377, 393; Michel, *Dissertation*, Göttingen, 1860; Moissan, *Compt. rend.*, 1896, 122, 1302; *Bull. Soc. chim.*, 1896, [3], 15, 1282; *Ann. Chim. Phys.*, 1896, [8], 9, 337; Wöhler and Michel, *Annalen*, 1860, 115, 102; Weiss, *Zeitsch. anorg. Chem.*, 1910, 65, 279; see also p. 184, this volume.

<sup>4</sup> Sargent, *J. Amer. Chem. Soc.*, 1900, 22, 783; Haynes, *J. Ind. Eng. Chem.*, 1913, 5, 189.

<sup>5</sup> Barrett, Brown, and Hadfield, *J. Inst. Elect. Eng.*, 1902, 31, 674.

<sup>6</sup> Haynes, *Eng. and Min. J.*, 1918, 105, 997.

<sup>7</sup> See *Engineering*, 1917, 104, 128; also Irmann, *Metall. und Erz.*, 1917, 14, 21, 37.

An alloy of tungsten with *gold* has been described,<sup>1</sup> as also have alloys of tungsten with *copper* and with *lead*.<sup>2</sup>

Tungsten and *antimony* are stated to unite, but tungsten and *bismuth* probably do not alloy.<sup>3</sup>

Alloys of tungsten with other elements are described in other volumes in this series.<sup>4</sup>

<sup>1</sup> Bernoulli, *Pogg. Annalen*, 1860, **III**, 573.

<sup>2</sup> Bernoulli, *loc. cit.*; Sargent, *J. Amer. Chem. Soc.*, 1900, **22**, 783; Inouye, *Mem. Coll. Sci. Kyoto*, 1920, **4**, 43.

<sup>3</sup> Bernoulli, *loc. cit.*; Sargent, *loc. cit.*

<sup>4</sup> The references to the literature are as follows: "W—Fe," Barrett, *Proc. Roy. Soc.*, 1902, **69**, 480; Barrett, Brown, and Hadfield, *loc. cit.*; Behrens and Lingens, *Verh. K. Akad. Wetensch. Amsterdam*, 1893–94, **2**, 151; Benneville, *J. Amer. Chem. Soc.*, 1894, **16**, 735; Bernoulli, *loc. cit.*; Carnot and Goutal, *Compt. rend.*, 1897, **125**, 148, 213; 1899, **128**, 207; *Ann. des Mines*, 1900, [9], **18**, 263; *Contributions à l'étude des alliages*, Paris, 1901, p. 493; Curie, *ibid.*, p. 157; Garrison, *J. Frank. Inst.*, 1891, **131**, 434; 1891, **132**, 54, 111; *Mon. scient.*, 1892, [4], **6**, 43, 274; Guillet, *Compt. rend.*, 1904, **139**, 519; Harkort, *Metallurgie*, 1907, **4**, 617, 639, 673; Koort, *Dingl. poly. J.*, 1888, **270**, 166, 211; Le Chatelier, *Contributions à l'étude des Alliages*, Paris, 1901, p. 413; Mathews, *Elec. World and Engineer*, 1902, **40**, 531; Merle, *Mon. scient.*, 1895, [4], **9**, 35; Norton, *J. Amer. Chem. Soc.*, 1897, **19**, 110; Osmond, *Compt. rend.*, 1887, **104**, 985; 1890, **110**, 242, 346; Poleck and Grützner, *Ber.*, 1893, **26**, 35; Schneider, *Oesterr. Zeitsch. Berg- und Hüttenwesen*, 1885, **33**, 257; Wahl, *J. Frank. Inst.*, 1892, **134**, 470; Honda and Murakami, *Sci. Rep. Tohoku Imp. Univ.*, 1918, **6**, 235; Daevs, *Zeitsch. anorg. Chem.*, 1921, **118**, 67; "W—Fe—Mn," Barrett, Brown, and Hadfield, *loc. cit.*; "W—Fe—Ti," Hamilton and Smith, *J. Amer. Chem. Soc.*, 1901, **23**, 151; "W—Ni," Bernoulli, *loc. cit.*; Sargent, *loc. cit.*; Trowbridge and Sheldon, *Amer. J. Sci.*, 1889, [3], **38**, 462; *Chem. News*, 1889, **60**, 312; Irmann, *Metall. und Erz*, 1915, **12**, 358; Vogel, *Zeitsch. anorg. Chem.*, 1921, **116**, 231; "W—Ni—Cu," Roberts-Austen, *Proc. Roy. Inst.*, 1893–95, **14**, 497; Irmann, *Metall. und Erz*, 1917, **14**, 21, 37; *Chem. Zentr.*, 1917, **1**, 1069; "W—Ni—Cu—Zn," Dewar and Fleming, *Phil. Mag.*, 1893, [5], **36**, 271; 1895, **40**, 95; Fleming, *Proc. Roy. Inst.*, 1896, **20**, 885; Irmann, *loc. cit.*; "W—Co," Haynes, *J. Ind. Eng. Chem.*, 1913, **5**, 189; Kreitz, *Metall. und Erz*, 1922, **19**, 137; "W—Mn," Arrivant, *Compt. rend.*, 1906, **143**, 594; "W—Mo," Geiss and van Liempt, *Zeitsch. anorg. Chem.*, 1923, **128**, 355.

## CHAPTER VII.

### COMPOUNDS OF TUNGSTEN.

#### GENERAL PROPERTIES OF TUNGSTEN COMPOUNDS.

In its compounds tungsten resembles molybdenum very closely. Like all the metals of the Group, it exhibits valency varying from 2 to 6, and its most stable derivatives are those containing hexavalent tungsten. Halogen compounds containing the element in all the various stages of oxidation are known, but in the oxygen derivatives the tungsten is found almost exclusively in the tetra- or hexa-valent condition. The dioxide  $\text{WO}_2$  is basic and gives with acids the corresponding series of salts, which, however, are unstable and readily undergo oxidation. With alkalis the dioxide liberates hydrogen and forms tungstates. The trioxide  $\text{WO}_3$  is an amphoteric oxide, but its acidic properties predominate. Its hydrate  $\text{WO}_3 \cdot \text{H}_2\text{O}$  or  $\text{H}_2\text{WO}_4$  is known as tungstic acid, and gives rise not only to a very stable series of normal tungstates, but also to several other series of salts which contain the ratio  $\text{R}'_2\text{O} : \text{WO}_3$  in varying proportions (see p. 208). The metatungstates, of composition  $\text{R}'_2\text{W}_4\text{O}_{13}$ , are known to be derived from a definite metatungstic acid,  $\text{H}_2\text{W}_4\text{O}_{13}$  (see p. 233).

Compounds intermediate between the di- and tri-oxides, and obtained from the latter by reduction, are known, and probably contain both tetra- and hexa-valent tungsten. These derivatives are generally blue in colour, and the existence of a definite blue oxide, of composition  $\text{W}_2\text{O}_5$ , appears to be established (see p. 199). Many of the blue reduction products appear to be mixtures of compounds in various stages of oxidation.

A remarkable series of reduction products is obtained from the tungstates of the alkali and alkaline earth metals. These have the empirical formula  $\text{R}'_2\text{O} \cdot (\text{WO}_3)_x \cdot \text{WO}_3$ , and are known as tungsten bronzes, since they are vividly coloured and usually possess a bronze-like superficial lustre (see p. 243).

More highly oxidised compounds corresponding to the persulphates and containing peroxidic oxygen are obtained by the action of hydrogen peroxide on tungstic acid and the tungstates (see p. 242).

Only two sulphides of tungsten,  $\text{WS}_2$  and  $\text{WS}_3$ , are known, but these dissolve in alkali solutions with formation of a series of soluble thio-salts (see p. 247).

Tungsten trioxide, like molybdenum trioxide, possesses in marked degree the property of combining with other acidic oxides, such as phosphorus pentoxide, arsenic pentoxide, silica, and boron trioxide, in varying proportions, producing heteropolyacids which contain the



tungsten in a complex anion, and which yield well-defined crystalline salts with basic oxides (see pp. 251-258, 264-268).

**Uses.**—Tungstic oxide and certain tungstates are used for imparting a yellow colour to glass and porcelain. Sodium tungstate has found application as a mordant, and for rendering fabrics more or less incombustible (see p. 228). The tungsten bronzes are used for decorative purposes.<sup>1</sup>

#### TUNGSTEN AND HYDROGEN.

No compound of tungsten with hydrogen is known to exist; the solubility of hydrogen in tungsten at temperatures up to 1500° C. is very small.<sup>2</sup>

#### TUNGSTEN AND FLUORINE.

Tungsten and fluorine react at ordinary temperatures with production of a volatile, white crystalline compound which is decomposed by water.<sup>3</sup>

**Tungsten Hexafluoride,  $WF_6$ ,** is obtained<sup>4</sup> by the action of anhydrous hydrogen fluoride upon tungsten hexachloride in platinum vessels, or by the interaction of antimony pentafluoride with the hexachloride. It is a solid at low temperatures; just above 0° C. it sublimes to a heavy gas which fumes in moist air; it reacts with water with production of tungstic acid. It attacks both glass and mercury; by alkalies it is decomposed, and with alkali fluorides it forms double salts.

**Oxyfluorides.**—The *oxyfluoride*,  $WOF_4$ , has been prepared<sup>5</sup> by interaction of the oxychloride,  $WOCl_4$ , with anhydrous hydrogen fluoride, and by heating tungsten trioxide with lead fluoride, bismuth fluoride, or cryolite. It forms small hygroscopic plates which are decomposed by water; it has the property also of absorbing in the cold half a molecule of ammonia, thereby becoming orange in colour.

Attempts to prepare the fluoride  $WO_2F_2$  by similar methods were unsuccessful, though small quantities are formed by the action of water on the oxytetrafluoride;<sup>5</sup> double compounds of the formulæ  $2KF.WO_2F_2.H_2O$ ,  $KF.WO_2F_2.H_2O$ ,  $2TlF.WO_2F_2$ ,  $3TlF.2WO_2F_2$ , and  $TlF.WO_2F_2$  have, however, been prepared.<sup>6</sup> The complex salt, luteocobaltic fluoroxytungstate,  $Co(NH_3)_6F_3.2WO_2F_2$ , may be obtained<sup>7</sup> by adding luteocobaltic fluoride to a solution of tungstic acid in hydrofluoric acid, and allowing to crystallise from the dilute acid solution. The crystals are stable at 110° C.

#### TUNGSTEN AND CHLORINE.

**Tungsten Dichloride.**—By careful reduction of tungsten hexachloride in hydrogen, or of the tetrachloride in carbon dioxide, there is

<sup>1</sup> Philipps, *Ber.*, 1882, 15, 499; Engels, *Zeitsch. anorg. Chem.*, 1903, 37, 125; Schaefer, *ibid.*, 1904, 38, 148.

<sup>2</sup> Sieverts and Bergner, *Ber.*, 1911, 44, 2394. The values obtained were not equilibrium values.

<sup>3</sup> The existence of double salts containing trivalent tungsten, e.g.  $KWF_4.H_2O$  and  $(NH_4)WF_4.H_2O$ , has been indicated by Rosenheim and Li, *Ber.*, 1923, 56, B, 2228.

<sup>4</sup> Ruff and Eisner, *Ber.*, 1905, 38, 742; *Zeitsch. anorg. Chem.*, 1907, 52, 256.

<sup>5</sup> Ruff and others, *Zeitsch. anorg. Chem.*, 1907, 52, 256.

<sup>6</sup> Ephraïm and Heymann, *Ber.*, 1909, 42, 4456; Marignac, *Ann. chim. Phys.*, 1863, [3], 69, 70.

<sup>7</sup> Miolati and Rossi, *Atti R. Accad. Lincei*, 1896, [5], 5, ii., 183, 223.

obtained<sup>1</sup> a grey, amorphous, non-volatile, though unstable mass, which appears to contain tungsten dichloride. The hexachloride is more readily reduced<sup>2</sup> by ignition in a stream of nitrogen with powdered aluminium and quartz;<sup>3</sup> on extracting the product with hydrochloric acid, and saturating the concentrated extract with hydrogen chloride, slender yellow needles, of composition  $\text{H}[\text{W}_3\text{Cl}_7 \cdot \text{H}_2\text{O}]_{\text{aq.}}$ , separate. This compound is less stable than the corresponding molybdenum compound, and rapidly loses hydrogen chloride on exposure to air. In alcoholic solution or on gentle heating, 1 molecule of hydrogen chloride is lost and an insoluble yellow residue of composition  $[\text{W}_3\text{Cl}_6 \cdot \text{H}_2\text{O}]$  remains. With concentrated sulphuric acid the compound  $\text{W}_3\text{Cl}_4(\text{SO}_4)$  is formed. A little water hydrolyses it to the compound  $[\text{W}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}]\text{Cl}_2$ ; much water or alkali hydroxides convert it completely to tungstic acid or tungstate. When the chlor-acid is dissolved in hot concentrated hydrobromic acid and the solution cooled, thin yellow leaflets, of composition  $\text{H}[\text{W}_3\text{Br}_4\text{Cl}_3 \cdot \text{H}_2\text{O}]\text{H}_2\text{O}$ , separate.

**Double Chlorides of Trivalent Tungsten**, with those of potassium, ammonium, rubidium, cesium, and thallium, have been prepared<sup>4</sup> by reduction with tin of a solution of potassium tungstate in concentrated hydrochloric acid. They are all anhydrous, of the type  $\text{R}_3\text{W}_2\text{Cl}_9$ , and are stable in the dry state. Conductivity and cryoscopic measurements show that the tungsten is present as part of a complex anion, and that in aqueous solution not more than four ions are produced by dissociation. The anion,  $\text{W}_2\text{Cl}_9'''$ , is very stable, and the chlorotungstates act as strong reducing agents on solutions of silver, gold, mercury, copper, and ferric salts; in the last case the reaction is quantitative. The following salts have been prepared:<sup>5</sup>

$\text{Cr}(\text{NH}_3)_6\text{W}_2\text{Cl}_9 \cdot 2\text{H}_2\text{O}$ , dark green, microscopic, rectangular prisms;  
 $\text{Co}(\text{NH}_3)_6\text{W}_2\text{Cl}_9 \cdot 6\text{H}_2\text{O}$ , bright green, microcrystalline powder;  
 $\text{Cu}(\text{NH}_3)_4\text{NH}_4\text{W}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ , and  
 $\text{Cu}(\text{NH}_3)_4\text{KW}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ , green crystalline powders;  
 $\text{Cd}(\text{NH}_3)_4\text{NH}_4\text{W}_2\text{Cl}_9$ ;  
 $\text{Cd}(\text{NH}_3)_4\text{KW}_2\text{Cl}_9$ ;  
 $[\text{Ag}(\text{NH}_3)_2]_3\text{W}_2\text{Cl}_9$ , unstable.

These are generally sparingly soluble in water, the concentrated solutions being green, the more dilute, yellow.

A solution of the free acid,  $\text{H}_3\text{W}_2\text{Cl}_9$ , is obtained by the action of hydriodic acid on a solution of the thallium salt; it has not, however, been isolated.<sup>5</sup>

**Tungsten Tetrachloride,  $\text{WCl}_4$ .** By partial reduction, with hydrogen, of the hexachloride, Riche<sup>6</sup> obtained this compound in the form of voluminous, greyish-brown crystals, which may be more readily obtained by distilling a mixture of the hexa- and penta-chlorides at a

<sup>1</sup> Roscoe, *Annalen*, 1872, **162**, 349; *Chem. News*, 1872, **25**, 61; *Bull. Soc. chim.*, 1872, **17**, 209.

<sup>2</sup> Lindner and co-workers, *Ber.*, 1922, **55**, [B], 1458; *Zeitsch. anorg. Chem.*, 1924, **140**, 357.

<sup>3</sup> Hill (*J. Amer. Chem. Soc.*, 1916, **38**, 2383) used sodium amalgam, but the reaction is difficult to control and the yield of tungsten dichloride is poor.

<sup>4</sup> Olsson, *Ber.*, 1913, **46**, 566; Rosenheim and Deln, *ibid.*, 1915, **48**, 1167.

<sup>5</sup> Collenberg and Sandved, *Zeitsch. anorg. Chem.*, 1923, **130**, 1.

<sup>6</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], **50**, 15. See Wöhler, *ibid.*, 1823, [2], **29**, 43; *Pogg. Annalen*, 1824, **2**, 345; von Borch, *J. prakt. Chem.*, 1851, **54**, 254; Roscoe, *loc. cit.*

low temperature in a current of hydrogen or carbon dioxide. It is also formed, together with other compounds, during the preparation of the pentachloride. It is infusible, but decomposes at a moderately high temperature into pentachloride and dichloride; if sufficiently heated, the ultimate *metallic* residue is pyrophoric. In presence of water the compound undergoes hydrolysis.<sup>1</sup>

A double hydroxychloride of tungsten with potassium chloride has been prepared<sup>2</sup> by the reduction with tin of a solution of potassium tungstate in concentrated hydrochloric acid; after a series of colour changes the compound  $K_2W(OH)Cl_5$ , which is stable in the dry condition, is obtained.

**Tungsten Pentachloride,  $WCl_5$ ,** is obtained by distillation in carbon dioxide of the lower chlorides produced by reduction of the hexachloride with hydrogen.<sup>3</sup> It is, in the amorphous state, a greyish substance, while its vapour is greenish yellow; in the crystalline condition it forms brilliant black needles. Tungsten pentachloride melts at  $248^\circ C.$  and boils at  $275.6^\circ C.$ ; its vapour density is normal.<sup>4</sup> It is hygroscopic, but is decomposed by excess of water, with production of the blue oxide and hydrogen chloride. Upon electrolysis of an alcoholic solution of tungsten hexa-chloride, the compound  $WCl_2(OEt)_3$ , containing pentavalent tungsten, is obtained.<sup>5</sup> Potassium and rubidium compounds, of composition  $R_2WOCl_5$ , probably containing pentavalent tungsten in a complex anion, have been described.<sup>6</sup>

**Tungsten Hexachloride,  $WCl_6$ .**—In the entire absence of air and of moisture, tungsten heated to redness combines with chlorine to form the hexachloride, but it is extremely difficult to prevent simultaneous formation of the readily volatile oxychloride  $WOCl_4$ ; <sup>7</sup> the reaction is accelerated catalytically by the presence of platinum black.<sup>8</sup> The hexachloride may also be obtained by the action of chlorine on the crystalline disulphide.<sup>9</sup> The compound is a violet substance crystallising, *e.g.* from solution in carbon disulphide, in the cubic system; it is only slowly decomposed by water, although as usually prepared it fumes in moist air and is decomposed by cold water owing to the presence of oxychlorides. It melts at  $275^\circ C.$  and boils at  $346^\circ C.$ ; <sup>10</sup> its mean vapour density at  $440^\circ C.$  is <sup>11</sup> 168.8, a value which points <sup>12</sup> to dissociation of the molecule at this temperature. As a matter of fact, dry carbon dioxide passed through the fused salt liberates chlorine from the hexachloride, but not from the pentachloride.

Reduction with hydrogen converts the hexachloride into lower chlorides (*q.v.*) and even into the metal (see p. 184), while with oxygen,

<sup>1</sup> Roscoe, *Annalen*, 1872, 162, 349.

<sup>2</sup> Olsson, *Ber.*, 1913, 46, 566.

<sup>3</sup> Blomstrand, *J. prakt. Chem.*, 1861, 82, 408; 1863, 89, 230. Cf. Malaguti, *Ann. Chim. Phys.*, 1835, [2], 60, 271, whose product was probably the oxychloride,  $WO_2Cl_2$ .

<sup>4</sup> Roscoe, *loc. cit.*; Blomstrand, *loc. cit.*

<sup>5</sup> Fischer and others, *Zeitsch. anorg. Chem.*, 1913, 81, 102, 170.

<sup>6</sup> Collenberg and Guthe, *Zeitsch. anorg. Chem.*, 1924, 134, 317; 136, 252.

<sup>7</sup> Blomstrand, *loc. cit.*; Roscoe, *loc. cit.*; Teclu, *Annalen*, 1877, 187, 225.

<sup>8</sup> Hill, *J. Amer. Chem. Soc.*, 1916, 38, 2383.

<sup>9</sup> Defacqz, *Compt. rend.*, 1899, 128, 609.

<sup>10</sup> Roscoe, *loc. cit.*; Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 15; Blomstrand, *loc. cit.*; Pring and Fielding, *Trans. Chem. Soc.*, 1909, 95, 1502.

<sup>11</sup> Roscoe, *loc. cit.*; Debray, *Compt. rend.*, 1865, 60, 820.

<sup>12</sup> Compare Persoz, *Ann. Chim. Phys.*, 1864, [4], 1, 93; *Compt. rend.*, 1864, 58, 1196; *Bull. Soc. chim.*, 1864, [2], 188.

oxychlorides are formed. With halogen hydracids, lower halides and mixed halides are formed.<sup>1</sup>

**Oxychlorides.**—Two oxychlorides of tungsten, respectively  $\text{WO}_2\text{Cl}_2$  and  $\text{WOCl}_4$ , are known.

*Tungsten dioxydichloride (tungstyl chloride)*,  $\text{WO}_2\text{Cl}_2$ , was originally considered<sup>2</sup> to be a chloride of tungsten, and was obtained, although mixed with a certain amount of the oxytetrachloride, by interaction of chlorine with tungsten dioxide.<sup>3</sup> In attempting to prepare tungsten hexa-chloride by the action of sulphur chloride<sup>4</sup> upon tungsten trioxide, Bourion<sup>5</sup> found that the product of the reaction was a mixture of the two oxychlorides only. Further, it is produced by heating tungsten hexachloride with oxalic acid.<sup>6</sup>

This oxychloride forms stable yellow crystals which readily sublime, but which also melt at  $259^\circ\text{C}$ .; at much higher temperatures the substance largely dissociates into tungstic anhydride and the oxytetrachloride. Partial decomposition is also effected by warming with water.<sup>7</sup>

*Tungsten oxytetrachloride*,  $\text{WOCl}_4$ , is obtained by heating tungsten pentachloride or hexachloride in oxygen,<sup>8</sup> by heating the pentachloride with oxalic acid,<sup>6</sup> by interaction of phosphorus pentachloride with tungsten trioxide;<sup>9</sup> together with the oxychloride,  $\text{WO}_2\text{Cl}_2$ , by heating tungsten trioxide in a current of sulphur chloride vapour,<sup>5</sup> by heating the trioxide or oxychloride,  $\text{WO}_2\text{Cl}_2$ , in the vapour of the hexachloride alone or mixed with chlorine,<sup>6</sup> or by passing dry chlorine over a heated mixture of tungsten trioxide and carbon,<sup>10</sup> the main product being then the oxytetrachloride, which may be obtained in a moderately pure state by taking advantage of its greater volatility than that of the dioxydichloride. It is also formed, together with small quantities of the hexachloride and probably of the pentachloride, when carbonyl chloride is passed over heated tungsten powder.<sup>11</sup>

Tungsten oxytetrachloride forms splendid transparent, ruby-red, needle-shaped crystals which melt at  $210^\circ\text{C}$ . and boil at  $227\cdot5^\circ\text{C}$ ., giving a red vapour of normal density.<sup>12</sup> By water it is decomposed, giving first the yellow oxychloride, and further, hydrochloric and tungstic acids. A certain amount of the yellow oxychloride is also formed from it by loss of chlorine on sublimation in air or oxygen.<sup>13</sup>

#### TUNGSTEN AND BROMINE.

Bromine and tungsten at a red heat interact directly;<sup>14</sup> bromides corresponding to the formulæ  $\text{WBr}_2$ ,  $\text{WBr}_5$ , and  $\text{WBr}_6$  are known.

<sup>1</sup> For details of these and other reactions, see Roscoe, *loc. cit.*; Blomstrand, *loc. cit.*; Defacqz, *Compt. rend.*, 1899, 128, 1232; 129, 515; *Ann. Chim. Phys.*, 1901, [7], 22, 238.

<sup>2</sup> Wöhler, *Ann. Chim. Phys.*, 1823, [2], 29, 43; *Pogg. Annalen*, 1824, 2, 345.

<sup>3</sup> Wöhler, *loc. cit.*; Roscoe, *Annalen*, 1872, 162, 349; *Chem. News*, 1872, 25, 61; *Bull. Soc. chim.*, 1872, 17, 209.

<sup>4</sup> Chlorine may also be used. See Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 15.

<sup>5</sup> Bourion, *ibid.*, 1910, [8], 21, 56.

<sup>6</sup> Debray, *Compt. rend.*, 1865, 60, 820.

<sup>7</sup> Riche, *loc. cit.*; Forcher, *J. prakt. Chem.*, 1862, 86, 408; *Bull. Soc. chim.*, 1863, 5, 197; Roscoe, *loc. cit.*

<sup>8</sup> Blomstrand, *loc. cit.*

<sup>9</sup> Schiff, *Annalen*, 1861, 117, 94; 1879, 197, 185.

<sup>10</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 15.

<sup>11</sup> Lindner and co-workers, *Ber.*, 1922, 55, [B], 1485.

<sup>12</sup> Riche, *loc. cit.*; Roscoe, *loc. cit.*

<sup>13</sup> Blomstrand, *J. prakt. Chem.*, 1861, 82, 408; 1863, 89, 230.

<sup>14</sup> von Borch, *ibid.*, 1851, 54, 254; Blomstrand, *loc. cit.*

**Tungsten Dibromide,  $WBr_2$ ,** remains as a velvety bluish-black crystalline residue when the pentabromide, heated in a bath of fused zinc chloride, is reduced by hydrogen.<sup>1</sup>

**Tungsten Pentabromide,  $WBr_5$ ,** is best prepared by passing a current of bromine vapour, which may be diluted with carbon dioxide, but must be entirely free from air and moisture, over tungsten at a red heat; <sup>2</sup> by heating the hexachloride at 300° C. in dry hydrogen bromide a less pure product results.

This compound forms lustrous dark brown hygroscopic crystals which melt at 276° C. and boil at 333° C., and which with excess water yield the blue oxide and hydrobromic acid, though they are insoluble in the common anhydrous organic solvents. They are reduced by hydrogen to the dibromide and to the pyrophoric metal; with oxygen, the oxybromides are formed.<sup>1</sup>

**Tungsten Hexabromide,  $WBr_6$ ,** is formed, in total absence of air and of moisture, by gently heating tungsten in bromine vapour in an atmosphere of nitrogen.<sup>3</sup> It sublimes, forming bluish-black needles which readily decompose on heating. It fumes in the air and is decomposed by water with formation of a blue oxide and hydrobromic acid.

**Chlorobromides.**—By treating tungsten hexachloride with liquidified hydrogen bromide at room temperatures, olive-green, hygroscopic crystals of the chlorobromide,  $WCl_6 \cdot WBr_6$ , are obtained, whereas the reaction at 60° to 70° C. produces the compound  $WCl_6 \cdot 3WBr_6$ , a crystalline substance possessing similar properties. The latter melts at 232° C.; both are readily decomposed by water.<sup>2</sup>

**Oxybromides.**—Two oxybromides of tungsten,  $WO_2Br_2$  and  $WOBr_4$ , are known. When bromine vapour is passed over red-hot tungsten dioxide, when a mixture of bromine vapour and air is passed over metallic tungsten, or when the pentabromide is passed over heated tungsten trioxide, both oxybromides are formed, and are separated by taking advantage of the fact that the oxybromide,  $WOBr_4$ , is the more readily volatile.<sup>4</sup>

The *dioxydibromide*,  $WO_2Br_2$ , forms light red, transparent, infusible crystals which yield a yellow powder; the vapour is slightly decomposed into the trioxide and the oxybromide,  $WOBr_4$ . It is unacted upon by cold water.

The *oxytetrabromide*,  $WOBr_4$ , forms readily fusible, dark brown lustrous needles of melting-point 277° C. and boiling-point 327° C. It is deliquescent and is decomposed by water.

#### TUNGSTEN AND IODINE.

**Tungsten Di-iodide,  $WI_2$ ,** is formed <sup>5</sup> on passing iodine vapour over the metal heated to redness,<sup>1</sup> or by heating the hexachloride at 400° to 450° C. in a current of dry hydrogen iodide.<sup>6</sup> The substance

<sup>1</sup> Roscoe, *Annalen*, 1872, 162, 349.

<sup>2</sup> Defacqz, *Compt. rend.*, 1899, 128, 1232; 1899, 129, 515; *Ann. Chim. Phys.*, 1900, [7], 22, 247.

<sup>3</sup> Schaffer and Smith, *J. Amer. Chem. Soc.*, 1897, 18, 1098; *Chem. News*, 1897, 75.

<sup>4</sup> Roscoe, *loc. cit.*; Bonnet, *Compt. rend.*, 1837, 4, 198; von Borch, *J. prakt. Chem.*, 1851, 54, 254.

<sup>5</sup> If no precautions are observed, a green substance which may be an oxyiodide is obtained.

<sup>6</sup> Defacqz, *loc. cit.*; also *Compt. rend.*, 1898, 126, 962.

brown in colour, amorphous, infusible, insoluble in water, alcohol, and carbon disulphide. It is decomposed if sufficiently heated.

**Tungsten Tetra-iodide,  $WI_4$ ,** has been prepared<sup>1</sup> by heating for two hours at 100° C. in a sealed tube a mixture of the hexachloride and liquefied hydrogen iodide. It is a black, crystalline, infusible substance which decomposes on volatilisation and has a density at 18° C. of 5.2. It is not completely stable in air; it is insoluble in water, ether, and chloroform.

#### TUNGSTEN AND OXYGEN.

Three well-defined oxides of tungsten exist: the brown, essentially basic, dioxide,  $WO_2$ ; the yellow, essentially acidic, trioxide,  $WO_3$ ; and a blue intermediate oxide, ditungsten pentoxide,  $W_2O_5$ . Several other oxides have been described, for example:  $W_4O_3$ ,  $W_2O_3$ ,  $W_5O_{14}$ ;<sup>2</sup>  $W_5O_8$ ;<sup>3</sup>  $W_3O_8$ ;<sup>4</sup> and  $W_4O_{11}$ ;<sup>5</sup> but the identity of none of these has been proved, and they appear to be either identical with, or mixtures containing, the blue oxide. By measurement of the equilibrium constants during reduction of the trioxide by a gradually increasing amount of hydrogen, it has been shown<sup>6</sup> that between the trioxide and the metal only the two oxides,  $W_2O_5$  and  $WO_2$ , exist as stable phases.

**Tungsten Dioxide,  $WO_2$ ,** may be obtained as a brown amorphous powder by heating the trioxide to dull redness in a current of hydrogen.<sup>7</sup> The residue remains in a stable condition, if allowed to cool in contact with hydrogen, for about twenty-four hours,<sup>8</sup> but it is difficult to obtain the pure dioxide by this means, as reduction is liable to proceed further unless the temperature is carefully regulated. It may also be produced by heating tungsten di-iodide to 500° C. in a current of carbon dioxide,<sup>9</sup> by acting on the tetrachloride with water,<sup>10</sup> or by heating a mixture of ammonium chloride and normal potassium tungstate, the residue being well washed with water.<sup>11</sup> In the wet way it is obtained as copper-red spangles by the addition of moderately strong hydrochloric acid and zinc to tungsten trioxide, to one of its hydrates,<sup>12</sup> or to sodium metatungstate.<sup>8</sup>

The crystalline form has been obtained<sup>13</sup> by heating lithium paratungstate in a current of hydrogen at about the melting-point of glass for forty-five minutes. The product, after cooling, was treated successively with boiling water, concentrated hydrochloric acid, and lithium hydroxide solution, and then very carefully washed with warm water; it remains as an opaque, brown, micro-crystalline powder, with a metallic lustre.

<sup>1</sup> Defacqz, *Compt. rend.*, 1898, **127**, 510.

<sup>2</sup> Desi, *J. Amer. Chem. Soc.*, 1897, **19**, 213; *Bull. Soc. chim.*, 1897, [3], **18**, 984; *Chem. Zentr.*, 1897, p. 797.

<sup>3</sup> Usler, *Annalen*, 1855, **94**, 225.

<sup>4</sup> von der Pfordten, *ibid.*, 1884, **222**, 137.

<sup>5</sup> Leiser, *Zeitsch. Elektrochem.*, 1907, **13**, 690.

<sup>6</sup> Wöhler and Balz, *ibid.*, 1921, **27**, 406.

<sup>7</sup> Berzelius, *Schweigger's J.*, 1816, **16**, 476; *Pogg. Annalen*, 1825, **4**, 147; 1826, **8**, 267.

<sup>8</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], **50**, 29.

<sup>9</sup> Defacqz, *Compt. rend.*, 1898, **126**, 962.

<sup>10</sup> Roscoe, *Annalen*, 1872, **162**, 349; *Bull. Soc. chim.*, 1872, **17**, 209; *Chem. News*, 1872, **25**, 61.

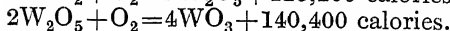
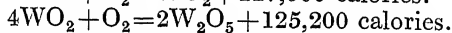
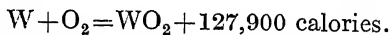
<sup>11</sup> Wöhler, *Ann. Chim. Phys.*, 1823, [2], **29**, 43; *Pogg. Annalen*, 1824, **2**, 345.

<sup>12</sup> Wöhler, *loc. cit.*; von der Pfordten, *Ber.*, 1883, **16**, 508; *Bull. Soc. chim.*, 1883, [2], **40**, 368; *Annalen*, 1884, **222**, 158.

<sup>13</sup> Hallopeau, *Compt. rend.*, 1898, **127**, 512; *Bull. Soc. chim.*, 1898, **19**, 748; *Ann. Chim. Phys.*, 1900, [7], **19**, 112.

The density of tungsten dioxide, according to Karsten, is 12.1109. It is stable in the air but is readily oxidised. Heated in oxygen, it yields the trioxide; at 500° C. in nitrous oxide or nitric oxide, the blue oxide,  $W_2O_5$ , results, while nitrogen peroxide yields the trioxide.<sup>1</sup>

The following thermal values have been determined: <sup>2</sup>



Heated in chlorine, the yellow oxychloride,  $WO_2Cl_2$ , is obtained.<sup>3</sup>

Tungsten dioxide thus acts as a powerful reducer, and will convert mercuric and cupric salts to the mercurous and cuprous condition,<sup>4</sup> and precipitate the metal from ammoniacal silver solutions.<sup>5</sup> The amorphous variety is soluble in hydrochloric and sulphuric acids, yielding red solutions which on standing undergo partial oxidation with loss of colour;<sup>6</sup> the crystalline dioxide is unacted upon, even by the hot concentrated acids.<sup>7</sup> Nitric acid has a slow oxidising action. Concentrated alkali solutions dissolve the amorphous oxide, with formation of the tungstate and liberation of hydrogen, but have no action on the crystalline variety.<sup>8</sup>

Tungsten dioxide is reduced to the metal by heating with carbon to about 1020° C.<sup>9</sup>

The corresponding *hydroxide*,  $W(OH)_4$ , has been prepared by the electrolytic reduction of solutions of tungsten trioxide in hydrochloric or hydrofluoric acid.<sup>10</sup> It is a brown powder, insoluble in sodium hydroxide, sulphuric acid, or acetic acid, but soluble in concentrated hydrochloric acid, yielding a greenish solution which rapidly becomes blue owing to oxidation of tetravalent tungsten to the pentavalent condition.

**The Blue Oxide of Tungsten (Ditungsten Pentoxide)** may be formed by oxidation of the dioxide, or by reduction of the trioxide. It is thus an intermediate oxide, and since it is itself prone to oxidation, it is difficult to isolate in a pure condition, and it is doubtful whether it has yet been so obtained. Our knowledge of its composition and properties is therefore limited. It is generally known as the "blue oxide" of tungsten, and there is evidence of pentavalent tungsten, but the blue product may also be regarded as essentially tungsten tungstate.

The formation of a blue compound by reduction of tungsten trioxide was first observed by Berzelius,<sup>11</sup> and the compound was first prepared by Malaguti<sup>12</sup> by heating the trioxide at 250° to 300° C. in a current of

<sup>1</sup> Sabatier and Senderens, *Ann. Chim. Phys.*, 1896, [7], 7, 348.

<sup>2</sup> van Liempt, *Zeitsch. anorg. Chem.*, 1923, 126, 226.

<sup>3</sup> Roscoe, *Annalen*, 1872, 162, 349; *Bull. Soc. chim.*, 1872, 17, 209; *Chem. News*, 1872, 25, 61.

<sup>4</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 29.

<sup>5</sup> Smith and Shinn, *Zeitsch. anorg. Chem.*, 1894, 7, 47.

<sup>6</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5.

<sup>7</sup> Hallopeau, *Comp. rend.*, 1898, 127, 512.

<sup>8</sup> Riche, *loc. cit.*; Hallopeau, *loc. cit.*; Delépine and Hallopeau, *Compt. rend.*, 1899, 129, 600.

<sup>9</sup> Greenwood, *Trans. Chem. Soc.*, 1908, 93, 1493.

<sup>10</sup> Bernhardt-Grisson, *Dissertation*, Berlin, 1910.

<sup>11</sup> *Lehrbuch der Chemie*, 3rd ed., 1833, ii., 365.

<sup>12</sup> Malaguti, *Ann. Chim. Phys.*, 1835, [2], 60, 271; *Compt. rend.*, 1835, 1, 292. See also Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5; Liesegang, *Photogr. Arch.*, 1865, p. 152.

hydrogen. Carbon monoxide may be used instead of hydrogen. The blue oxide may also be obtained by cautiously heating ammonium paratungstate in a closed crucible,<sup>1</sup> by the electrolysis of fused sodium tungstate<sup>2</sup> or of a boiling solution of a tungstate in hydrochloric acid,<sup>3</sup> by decomposition of tungsten pentachloride or pentabromide by means of water,<sup>4</sup> or by reduction of an acidified solution of a tungstate by means of zinc or stannous chloride. The product is a powder of which the colour varies from greenish blue to deep blue. It is readily converted to the trioxide by heating in oxygen or air. Its magnetic susceptibility is <sup>5</sup> 0.755. When prepared in the wet way it is readily oxidised by nitric acid, but the product obtained in the dry way resists this reagent.

A similar blue compound was prepared by Allen and Gottschalk<sup>6</sup> by heating on a water-bath a mixture of tungsten trioxide and stannous chloride in hydrochloric acid solution, or by heating the trioxide with concentrated hydriodic acid in a sealed tube at 200° C. The product was oxidised on standing in air, was insoluble in hydrochloric acid, but soluble in alkalis with evolution of hydrogen. Its composition appeared to be  $W_5O_{14} \cdot H_2O$ . It reacted with ammonia, yielding some ammonium tungstate and a brownish-purple residue of composition  $W_3O_8 \cdot H_2O$ .

A colloidal solution of the blue oxide, known as *tungsten blue*, may be obtained by the electrolytic reduction of an acidified tungstate solution,<sup>7</sup> or by first saturating a solution of metatungstic acid with hydrogen sulphide and then neutralising by means of ammonia or ammonium sulphide.<sup>8</sup> The solution, when freshly prepared, is optically void, but, on standing, a luminous cone gradually appears.<sup>9</sup> Under the influence of the electric current the colloid moves towards the anode. The composition of the dissolved oxide, according to Leiser, is  $W_4O_{11}$ . The solution may be used for dyeing silk, and also, but not so satisfactorily, cotton and wool.

**Tungsten Trioxide, Tungstic Anhydride, or "tungstic acid,"**  $WO_3$ , occurs naturally as *tungstite* (see p. 182), but it is usually obtained from the commoner ores, *scheelite* and *wolframite*. Scheelite is readily decomposed by means of hydrochloric acid or nitric acid,<sup>10</sup> and on washing and igniting the residue, tungsten trioxide results. Wolframite is more resistant to acid attack,<sup>11</sup> but by treating the finely powdered ore first with hydrochloric acid and then with aqua regia, the iron and manganese may be dissolved out, and the residue on addition of ammonia will yield a solution from which crystals of ammonium tungstate can be obtained on concentration, and these on heating yield the trioxide.<sup>12</sup>

<sup>1</sup> Malaguti, *loc. cit.*; Usler, *Beiträge zur Kenntnis des Wolframs und Molybdäns*, Göttingen, 1855; Desi, *J. Amer. Chem. Soc.*, 1897, 19, 213.

<sup>2</sup> Burckhard, *Zeitsch. Chem.*, 1870, 6, 212. <sup>3</sup> Smith, *Ber.*, 1880, 13, 753.

<sup>4</sup> Roscoe, *Annalen*, 1872, 162, 363.

<sup>5</sup> Wedekind and Horst, *Ber.*, 1915, 48, 105.

<sup>6</sup> Allen and Gottschalk, *Amer. Chem. J.*, 1902, 27, 328.

<sup>7</sup> Leiser, *Zeitsch. Elektrochem.*, 1907, 13, 690.

<sup>8</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273; Biltz, *Ber.*, 1904, 37, 1095; Biltz and Geibel, *Nachr. Ges. Wiss.*, Göttingen, 1906, p. 141.

<sup>9</sup> Biltz and Geibel, *loc. cit.* <sup>10</sup> Nordenskjöld, *Pogg. Annalen*, 1861, 114, 612.

<sup>11</sup> Weiss, Martin, and Stimmelmayer, *Zeitsch. anorg. Chem.*, 1910, 65, 279.

<sup>12</sup> Schneider, *J. prakt. Chem.*, 1850, 50, 154; von Borch, *ibid.*, 1851, 54, 254; Lotz, *Annalen*, 1854, 91, 51; Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 33; Marignac, *ibid.*, 1863, [3], 69, 12; Persoz, *ibid.*, 1864, [4], 1, 97.



It is more usual, however, to effect the decomposition of wolframite by fusion with alkali according to one of the following methods :

1. The ore is fused with twice its weight of potassium carbonate and the resulting mass digested with water. Ammonium chloride is added to the aqueous extract<sup>1</sup> and the solution evaporated to dryness, the residue being ignited to drive off the ammonium salt; potassium chloride is next removed by washing with hot water, and any acid potassium tungstate remaining is removed by boiling with dilute potassium hydroxide, leaving a residue of tungsten dioxide which after thorough washing with water is converted to the trioxide by ignition in an open crucible.

2. Powdered wolframite is fused with sodium carbonate and sodium nitrate, and after cooling, sodium tungstate is extracted from the mass with water, leaving a residue containing iron, manganese, calcium, and any columbium, tantalum, or tin that may have been present in the mineral. Crystallisation of the solution yields the dihydrate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,<sup>2</sup> or if the hot solution is first nearly neutralised by means of nitric acid or hydrochloric acid, sodium paratungstate (see p. 228) can be crystallised out.<sup>3</sup> The oxide may then be obtained directly from either of these compounds (see p. 203).

3. An intimate mixture of the ore with chalk and sodium chloride or calcium chloride,<sup>4</sup> or with calcium chloride alone,<sup>1</sup> is heated to about  $600^\circ$  to  $700^\circ$  C.; or the ore may be first fused with sodium hydrogen sulphate, and then with lime or a calcium salt.<sup>5</sup> The residue is powdered and treated with boiling concentrated hydrochloric acid, which decomposes the tungstate with precipitation of tungsten trioxide.

Other methods of extraction are applicable on a smaller scale. When a mixture of powdered ore and quartz is heated in a stream of carbon tetrachloride vapour, a distillate is obtained of tungsten chloride, which may be decomposed by acid<sup>6</sup> (see p. 270). Solutions of tungstates, such as are obtained as a by-product from zinc minerals containing tungsten, may be decomposed with hydrochloric acid.<sup>7</sup>

*Preparation of Pure Tungsten Trioxide.*—The oxide prepared by any of the above processes is always impure, the nature of the impurities depending on the composition of the ore and on the materials employed in the process. If alkali has been used, the presence of sodium, potassium, or calcium tends to give the product a greenish appearance.<sup>8</sup> Iron, manganese, silica, phosphorus, tin, molybdenum, vanadium, and columbium may all be present, and since tungsten is prone to form complex compounds with many of these, the purification of the oxide is not easily accomplished.

Probably the most satisfactory method is that of Smith and Exner,<sup>9</sup>

<sup>1</sup> Wöhler, *Pogg. Annalen*, 1824, 2, 345.

<sup>2</sup> Zettnow, *ibid.*, 1867, 130, 16, 241.

<sup>3</sup> Bernoulli, *ibid.*, 1860, 111, 576; Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>4</sup> Weiss, Martin, and Stimmelmayer, *Zeitsch. anorg. Chem.*, 1910, 65, 279; Jean, *Compt. rend.*, 1875, 81, 95; *Bull. Soc. chim.*, 1876, [2], 25, 65.

<sup>5</sup> Clotten, *German Patent*, 141811 (1902); Brandenburg and Weyland, *German Patent*, 149556 (1902).

<sup>6</sup> Jannasch and Leiste, *German Patent*, 266973 (1913).

<sup>7</sup> Philipp, *Jahresber.*, 1875, p. 745; Franz, *J. prakt. Chem.*, 1871, [2], 4, 238.

<sup>8</sup> Roscoe, *Chem. News*, 1872, 25, 90; Smith and Lukens, *ibid.*, 1926, 132, 33.

<sup>9</sup> Smith and Exner, *ibid.*, 1904, 90, 37, 49, 66.

which consists in digesting ammonium tungstate with nitric acid (1 : 1) and a little hydrochloric acid, and after thoroughly washing the tungsten trioxide produced, dissolving it in ammonia, and allowing the paratungstate to crystallise out. After repeating the process several times pure paratungstate is obtained. This salt, on further digesting with nitric acid and then evaporating to complete dryness, yields pure tungsten trioxide.<sup>1</sup>

Silica may be removed from impure tungstic anhydride by fusion with potassium hydrogen sulphate<sup>2</sup> and extraction of the alkali tungstate from the cooled mass with water.

Molybdenum may be separated as sulphide by passing hydrogen sulphide into a solution of the oxide in hydrochloric acid containing tartaric acid.<sup>3</sup> This method is not effective with large quantities, and it is better to convert the trioxide to sodium tungstate (see p. 225), dissolve in water, and nearly neutralise with hydrochloric acid, when the paratungstate can be crystallised out.<sup>4</sup> One half of it is dissolved in boiling water and the trioxide precipitated by the addition of hydrochloric and a little nitric acid.<sup>5</sup> The precipitate is then added to a boiling solution of the other half of the paratungstate and the boiling continued until complete transformation into the metatungstate occurs and hydrochloric acid no longer gives a precipitate. The acidified solution is then treated with hydrogen sulphide, when all the molybdenum is precipitated.

Finely powdered sodium tungstate or paratungstate, or a concentrated solution of the latter, when treated with a large excess of boiling hydrochloric acid (1 : 1) containing a little nitric acid, yields a voluminous orange-coloured mass from which the trioxide may be obtained by ignition. A similar product remains when the tungstate or paratungstate is heated with concentrated sulphuric acid in a porcelain dish until the acid fumes strongly, the mixture after cooling being diluted with water and washed by decantation.<sup>6</sup>

The precipitation from dilute solutions of sodium tungstate by the addition of mineral acids has been investigated by optical methods by Lottermoser,<sup>7</sup> whose results indicate that the process is auto-catalytic. The velocity of the reaction depends upon the hydrogen-ion concentration, the change taking place more rapidly with hydrochloric acid than with sulphuric acid, whilst acetic acid does not cause precipitation.

As obtained by any of the above methods, tungsten trioxide is a bright canary-yellow coloured amorphous powder, which becomes dark orange when heated, but regains its bright yellow colour on cooling. It has also been obtained in the crystalline form : (1) by strongly heating amorphous tungsten trioxide ;<sup>8</sup> (2) by fusion of hydrated tungsten trioxide with borax ;<sup>9</sup> (3) by passing hydrogen chloride over tungsten

<sup>1</sup> See also Persoz, *Ann. Chim. Phys.*, 1864, [4], i, 93 ; Bernoulli, *Pogg. Annalen*, 1860, **III**, 590 ; Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 15.

<sup>2</sup> Waddell, *Amer. Chem. J.*, 1886, 8, 280.

<sup>3</sup> Waddell, *loc. cit.* ; Wöhler and Engels, *Koll. Chem. Beihefte*, 1910, i, 454.

<sup>4</sup> Friedheim and Meyer, *Zeitsch. anorg. Chem.*, 1892, i, 76.

<sup>5</sup> Cf. Persoz, *loc. cit.*

<sup>6</sup> Zettnow, *Pogg. Annalen*, 1860, **III**, 16 ; 1867, **130**, 16, 241.

<sup>7</sup> Lottermoser, *Kolloid. Zeitsch.*, 1914, **15**, 145.

<sup>8</sup> Bernoulli, *Pogg. Annalen*, 1860, **III**, 576 ; Schafarik, *Sitzungsber. K. Akad. Wiss. Wien*, 1863, 47, 246.

<sup>9</sup> Nordenskjöld, *Pogg. Annalen*, 1861, **114**, 612.

trioxide heated to bright redness ;<sup>1</sup> or (4) by strongly heating a mixture of sodium tungstate and sodium carbonate in a stream of hydrogen chloride.<sup>1</sup> According to Nordenskjöld, the crystals obtained were small transparent prisms of the orthorhombic system :

$$a : b : c = 0.6966 : 1 : 0.4026 ;$$

those obtained by Debray were octahedral, some yellow and translucent, others dark green and opaque.<sup>2</sup>

Tungsten trioxide may also be obtained by direct synthesis. When a tungsten wire is heated in oxygen at low pressure, the trioxide is formed at about 800° Abs.;<sup>3</sup> above this temperature the oxide volatilises and the metal is left clean and bright at 1200° Abs.

The density of amorphous tungsten trioxide at 17° C. is 7.16 ;<sup>4</sup> whilst that of the crystalline variety at the same temperature is 7.23.<sup>5</sup> The specific heat of the trioxide between 8° C. and 98° C. was determined by Regnault<sup>6</sup> to be 0.0798. The following values for lower temperatures have been determined more recently :<sup>7</sup>

Temperature Range, ° C.	Specific Heat.	Molecular Heat.
—189.0 to —80.9	0.0442	10.25
— 75.8 to 0.0	0.0678	15.73
+ 2.3 to +46.6	0.0783	18.16

When heated, tungsten trioxide fuses at a temperature between 1300° and 1400° C.,<sup>8</sup> but, unlike the trioxide of uranium (see p. 305), no change in composition occurs up to 1750° C.<sup>9</sup> It is more strongly magnetic than metallic tungsten (see p. 187), its magnetic susceptibility at 15° C. being 0.808.<sup>10</sup> The compound readily undergoes reduction; the greenish tinge which the powder sometimes possesses, if not due to metallic impurity (*cf.* p. 202), is due to reduction at ordinary temperatures by traces of organic matter,<sup>11</sup> lower oxides being formed; the yellow colour may be restored by heating in a current of oxygen. When heated with carbon, tungsten trioxide yields the blue oxide between 650° and 850° C., a dark brown mixture of oxides between 900° and 1050° C., and metallic tungsten above 1050° C.;<sup>12</sup> if hydrogen is used as the reducer, the mixture of brown oxides is obtained at 800° to 900° C., and at 1080° C. a deposit of pure tungsten (99.4 per cent.) results. The metal

<sup>1</sup> Debray, *Compt. rend.*, 1862, 55, 287.

<sup>2</sup> See also Burger, *Zeitsch. anorg. Chem.*, 1922, 121, 240.

<sup>3</sup> Langmuir, *J. Amer. Chem. Soc.*, 1913, 35, 105.

<sup>4</sup> Zettnow, *Pogg. Annalen*, 1867, 130, 16, 241; Smith and Exner, *Chem. News*, 1904, 90, 66.

<sup>5</sup> Zettnow, *loc. cit.* Nordenskjöld gives density varying from 6.302 to 6.384.

<sup>6</sup> Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129; *Pogg. Annalen*, 1841, 53, 60, 243. Kopp, *Annalen Suppl.*, 1864, 3, 1, gives value 0.0894.

<sup>7</sup> Russell, *Physikal. Zeitsch.*, 1912, 13, 59.

<sup>8</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5.

<sup>9</sup> Read, *Trans. Chem. Soc.*, 1894, 65, 313.

<sup>10</sup> Wedekind and Horst, *Ber.*, 1915, 48, 105.

<sup>11</sup> van Liempt, *Zeitsch. anorg. Chem.*, 1921, 119, 310.

<sup>12</sup> Davis, *J. Ind. Eng. Chem.*, 1919, 11, 201.

is also produced when the oxide is heated with aluminium or zinc (see p. 184).

If hydrogen is passed through water at  $85^{\circ}$  C. and the mixture of hydrogen and water vapour then passed over tungstic anhydride at  $900^{\circ}$  C., the latter is reduced to the dioxide,  $\text{WO}_2$ .<sup>1</sup> The reaction is influenced by the amount of water vapour present, and the pentoxide,  $\text{W}_2\text{O}_5$ , results when the temperature of the water is maintained at  $97^{\circ}$  C.

Tungsten trioxide is insoluble in water and in most acids, including aqua regia, but is dissolved by hydrofluoric acid. It is also soluble in solutions of alkali hydroxides and carbonates yielding tungstates.

It is acted upon by chlorine, the yellow oxychloride,  $\text{WO}_2\text{Cl}_2$  (see p. 197), being formed; hydrogen sulphide gives the sulphide; gaseous ammonia reacts to form the oxy-amidonitride.<sup>2</sup>

The trioxide remains unchanged when heated in a current of nitric oxide; it is reduced to lower oxides by ethylene or acetylene at red heat, by methane at a higher temperature, and by phosphine at  $125^{\circ}$  to  $150^{\circ}$  C.<sup>3</sup> Heated with phosphorus pentachloride in an atmosphere of carbon dioxide it yields a red-brown product which consists of a mixture of tungsten chlorides and oxychlorides.<sup>4</sup>

Tungsten trioxide may be used as a yellow colouring matter in the ceramic industry, since permanent yellow glazes can be produced by fusion at  $800^{\circ}$  C. with lead silicate, with bismuth oxide, or with a mixture of zinc borate and silicate.<sup>5</sup>

**Hydrates of Tungsten Trioxide, Tungstic Acid.**—Two well-defined hydrates of tungsten trioxide are known :

1. A yellow *monohydrate*,  $\text{WO}_3 \cdot \text{H}_2\text{O}$ , and
2. A white *dihydrate*,  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ . With bases, both hydrates produce the same series of salts, and the first appears to be the true acid, tungstic acid,  $\text{H}_2\text{WO}_4$ , whilst the second is the hydrate,  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ . Both are insoluble in water, but colloidal forms of the acid exist. Several other hydrates have been described,<sup>6</sup> but except in the case of the complex hydrate known as metatungstic acid (see p. 233) their existence has not been established.

*Tungstic acid*,  $\text{H}_2\text{WO}_4$ , is formed as an amorphous yellow precipitate when an excess of *hot* hydrochloric acid is added to a solution of an alkali tungstate. If cold acid is used a white precipitate of the hydrate,  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ , results,<sup>7</sup> from which the acid may be obtained either by boiling the mixture or by drying over sulphuric acid. It may also be prepared by the following methods :

(i) By digesting a tungsten mineral with hydrochloric acid and then with aqua regia until the iron and manganese are dissolved and a yellow residue remains. This, after washing, is shaken with ammonia, which dissolves the free tungstic acid. The liquid is filtered, and on concentration tungstic acid crystallises out.

<sup>1</sup> van Liempt, *Zeitsch. anorg. Chem.*, 1923, 126, 183, 226. See also Wöhler and Günther, *Zeitsch. Elektrochem.*, 1923, 29, 276; Reinders and Verloet, *Rec. Trav. Chim.*, 1923, 42, 625.

<sup>2</sup> Wöhler, *Ann. Chim. Phys.*, 1850, [3], 29, 187; *Annalen*, 1850, 73, 191.

<sup>3</sup> Ehrenfeld, *J. Amer. Chem. Soc.*, 1895, 17, 381; *Bull. Soc. chim.*, 1895, [3], 14, 919.

<sup>4</sup> Schiff, *Annalen*, 1861, 117, 94; 1879, 197, 185; Ehrenfeld, *loc. cit.*

<sup>5</sup> Granger, *Compt. rend.*, 1905, 140, 935.

<sup>6</sup> See Laurent, *ibid.*, 1847, 25, 538; *Ann. Chim. Phys.*, 1847, [3], 21, 54; Schaefer, *Zeitsch. anorg. Chem.*, 1904, 38, 142.

<sup>7</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 15.

(ii) By heating the mineral under pressure with concentrated potash solution and lime, the tungstic acid being subsequently separated from the resulting solution by fractional precipitation.<sup>1</sup>

(iii) By fusion of the finely powdered mineral with alkali carbonates, sodium chloride, or calcium chloride. The residue is treated with water and then with nitric or hydrochloric acid to decompose any insoluble tungstates. The acid may be further purified by solution in ammonia and precipitation with dilute nitric acid,<sup>2</sup> or by means of chlorine.<sup>3</sup>

The *white hydrate*,  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ , is produced by the decomposition of tungsten pentachloride, or the oxychlorides, in presence of moist air.<sup>4</sup>

Both hydrates on heating to  $100^\circ$  to  $110^\circ$  C. lose water and leave a residue of composition  $2\text{WO}_3 \cdot \text{H}_2\text{O}$ .<sup>5</sup> This does not appear to be a true hydrate; on further heating, anhydrous  $\text{WO}_3$  is obtained, and the process of dehydration has been investigated by means of the Hüttig tensi-eudiometer, an instrument which is able to determine the pressure and volume of a gas liberated in any reaction at any moment.<sup>6</sup> The results indicate that between the dihydrate,  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , and the anhydrous compound only one definite hydrate,  $\text{WO}_3 \cdot \text{H}_2\text{O}$ , exists.<sup>7</sup> These results are supported by X-ray examination, both hydrates exhibiting characteristic crystalline forms.<sup>8</sup>

The yellow hydrate dissolves very slightly in water; the specific conductivity of the saturated solution at  $25^\circ$  C. is  $\kappa = 10.3 \times 10^{-6}$ .

Tungstic acid is insoluble in most acids, but dissolves slightly in hydrochloric acid<sup>10</sup> and is readily soluble in hydrofluoric acid,<sup>11</sup> as is shown in the following table:

Solvent.	Temperature, ° C.	Grams $\text{WO}_3$ in 100 Grams Solution.
Hydrofluoric acid (40 per cent. HF)	25	44.75
Hydrochloric acid (38 per cent. HCl)	50	53.7
" " "	50	0.36
" " "	80	0.75

It is readily soluble in alkalis.

**Colloidal Tungstic Acid.**—When dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid,

<sup>1</sup> French Patent, 389040 (1908); *J. Soc. Chem. Ind.*, 1908, 27, 939.

<sup>2</sup> U.S. Patent, 926084 (1909); *J. Soc. Chem. Ind.*, 1909, 28, 794.

<sup>3</sup> Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 144.

<sup>4</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 15; Forcher, *J. prakt. Chem.*, 1862, 86, 408; *Bull. Soc. chim.*, 1863, 5, 197.

<sup>5</sup> Braun, *J. prakt. Chem.*, 1864, 91, 396.

<sup>6</sup> Hüttig, *Zeitsch. anorg. Chem.*, 1920, 140, 161.

<sup>7</sup> Hüttig and Kurre, *ibid.*, 1922, 122, 44.

<sup>8</sup> Burger, *ibid.*, 1922, 121, 240.

<sup>9</sup> Wells, *J. Amer. Chem. Soc.*, 1907, 29, 112.

<sup>10</sup> Mallet, *Ber.*, 1875, 8, 831.

<sup>11</sup> Bernhardt-Grisson, *Dissertation*, Berlin, 1910; Rosenheim and Bernhardt-Grisson, *VIIth Inter. Congr. Appl. Chem.*, 1911, Section X, p. 120.

a colloidal solution of tungstic acid is obtained (*cf.* p. 241).<sup>1</sup> If the solution of sodium tungstate is concentrated, a white gelatinous precipitate is obtained on the addition of the acid. This precipitate, after washing by decantation at a low temperature (0° to 5° C.) with as little exposure to air as possible, may be dissolved in a concentrated solution of oxalic acid and the liquid subjected to dialysis. If the outer water is repeatedly changed, the oxalic acid may be completely removed, leaving a colloidal solution of tungstic acid.<sup>2</sup>

The colloidal solution may also be prepared by dissolving tungsten tetrachloride in alcohol and ether (equal volumes) and then diluting with alcohol and water.<sup>3</sup> The solution obtained acts as a positive colloid and coagulates immediately when small quantities of neutral salts, hydroxides, or strong acids are added. On passing an electric current through the solution, a deep blue precipitate separates at the cathode.<sup>4</sup>

A hydrosol of tungsten hydroxide is readily produced by the electrolysis of a 2 per cent. solution of sodium tungstate between a mercury cathode and a silver anode in a Hildebrand cell. The solution must not be allowed to become acid, or blue compounds are produced. The hydrosols obtained in this way are clear and transparent but brown in colour. The addition of potassium chloride causes coagulation, a black powder, resembling the lower oxides of tungsten, being formed.<sup>5</sup>

Colloidal solutions of tungstic acid, in presence of various organic reducing agents such as formaldehyde, sucrose, glucose, dextrin, etc., yield intensely blue solutions on exposure to light. If the solution is kept for some time, it does not undergo this reduction on being exposed to light; but on raising the temperature the blue reduction products are obtained. In order to account for this it has been suggested<sup>6</sup> that two forms of colloidal tungstic acid exist, one being photochemically sensitive and the other not. The former changes spontaneously into the latter, the reverse change being brought about by rise in temperature, and the absorption spectra of the two modifications differ considerably.

The composition of the hydrosol has not been determined, but it is thought to consist of tungstic acid in combination with water, or possibly with sodium tungstate, since Sabanéeff obtained an amorphous powder, of composition  $\text{Na}_2\text{O} \cdot 4\text{WO}_3$ , from the dialysed solution.

When the solution is evaporated to dryness, transparent vitreous scales remain, strongly adherent to the crucible; on heating this residue to redness, the trioxide  $\text{WO}_3$  results. The aqueous solution has a bitter astringent taste; its density at 19° C. is as follows:<sup>7</sup>

Per cent. $\text{WO}_3$ ,	5	20	50	66.5	79.8
Density,	1.0475	1.2168	1.8011	2.396	3.243.

<sup>1</sup> Graham, *J. Chem. Soc.*, 1864, 17, 318; *Ann. Chim. Phys.*, 1864, [4], 3, 128; *Compt. rend.*, 1864, 59, 174; *Bull. Soc. chim.*, 1864, 2, 185; Sabanéeff, *Zeitsch. anorg. Chem.*, 1897, 14, 354; Pappadà, *Gazzetta*, 1902, 32, [2], 22; Lottermoser, *Verh. Ges. deut. Naturforsch. Aerzte*, 1910, ii., 70; Vasilieva, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 819; *Zeitsch. wiss. Photochem.*, 1913, 12, 1.

<sup>2</sup> Pappadà, *loc. cit.*

<sup>3</sup> Müller, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 93.

<sup>4</sup> Müller, *loc. cit.*; Wöhler and Engels, *Zeitsch. Elektrochem.*, 1910, 16, 693.

<sup>5</sup> Kröger, *Kolloid Zeitsch.*, 1922, 30, 16.

<sup>6</sup> Vasilieva, *loc. cit.*

<sup>7</sup> Graham, *loc. cit.*

The gelatinisation of silicic acid is retarded by the presence of colloidal tungstic acid.<sup>1</sup>

### SALTS OF TUNGSTIC ACID.

Tungstic acid resembles molybdic acid in that it reacts with bases to form many different types of salts. A satisfactory classification of these salts has long been, and still is, a matter of difficulty, owing to the fact that many of the compounds are only described by individual investigators, whose work is either insufficient in detail or has lacked confirmation by later workers. The existence of the di- and tri-tungstates prepared by Lefort<sup>2</sup> has not been established.<sup>3</sup> Laurent, in 1847,<sup>4</sup> suggested that there were at least five distinct acids (combinations of tungstic anhydride with water in different proportions) with corresponding series of salts, and although the preparation and properties of all these acids have been described,<sup>5</sup> it is now recognised, largely owing to the work of Riche, Scheibler, and Marignac, that only two different acids are definitely known to exist, namely, ordinary tungstic acid,  $\text{H}_2\text{WO}_4$ , and metatungstic acid,  $\text{H}_2\text{W}_4\text{O}_{13}\cdot\text{aq.}$  (see p. 236). The former is insoluble in water and reacts with bases to form normal di-, tri-, and para-tungstates; the latter is soluble in water and yields a well-defined series of salts, the metatungstates.

This division into only two groups is justified by the fact that the metatungstates show marked differences both in properties and in ionic reactivity from those of the ordinary normal and acid tungstates, whilst the latter are very similar in their reactions. The transformation of normal tungstates into ordinary acid tungstates takes place readily, whereas the formation of metatungstates—by the addition of tungstic acid or other acids to tungstates—takes place only slowly and incompletely at ordinary temperatures. Further differences between the two types of salts are found in the peculiar behaviour of metatungstates on dehydration (see p. 234), and in the fact that whilst normal and paratungstates increase the specific rotatory power of tartaric acid, the metatungstates do not act in this way.<sup>6</sup>

Of the numerous types of salts of ordinary tungstic acid only two (the *normal*, of composition  $\text{R}_2\text{O}\cdot\text{WO}_3\cdot x\text{H}_2\text{O}$ , and the so-called *para-tungstates* in which the ratio  $\text{R}_2\text{O} : \text{WO}_3 = 3 : 7$  or  $5 : 12$ ) have been accurately investigated and their existence established beyond doubt. The readiness with which one type of salt is transformed into another, and the fact that paratungstates decompose on prolonged contact with water or on heating, make exact analysis almost impossible; and an added difficulty lies in the high atomic weight of tungsten, the difference in composition of various compounds with high tungsten content being very small. It is from such causes that, although the paratungstates are recognised as a well-defined series of salts, their actual constitution

<sup>1</sup> Graham, *J. Chem. Soc.*, 1864, 17, 318; Kröger, *Kolloid Zeitsch.*, 1922, 30, 16.

<sup>2</sup> Lefort, *Compt. rend.*, 1878, 87, 748; 1879, 88, 798; *Ann. Chim. Phys.*, 1878, [5], 15, 321; 1879, [5], 17, 470.

<sup>3</sup> Kantschew, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 729.

<sup>4</sup> Laurent, *Ann. Chim. Phys.*, 1847, [3], 21, 54; *Compt. rend.*, 1847, 25, 538.

<sup>5</sup> Laurent, *loc. cit.*; Hallopeau, *Compt. rend.*, 1895, 121, 61; *Ann. Chim. Phys.*, 1900, [7], 19, 135; Gerber, *Mon. scient.*, 1917, [5], 7, 73, 121, 169, 219; see Barbe, *ibid.*, 1919, [5], 9, i., 73.

<sup>6</sup> Rosenheim and Itzig, *Ber.*, 1900, 33, 707.

and relation to the normal tungstates remains unestablished (see below). Further, the higher acid salts such as hexa- and octa-tungstates appear to show a closer relation to meta-tungstates than to ordinary tungstates, but the nature of this has not been determined. According to Smith,<sup>1</sup> tungstates of the type  $4R_2O \cdot 10WO_3 \cdot xH_2O$  constitute another very definite series of salts.

The **normal tungstates** of the alkali metals are usually obtained by fusing together tungstic anhydride and the alkali hydroxide or carbonate in equivalent proportions. Those of the heavier metals are produced either by double decomposition in solution, or by fusing together an alkali tungstate and the chloride of the metal,<sup>2</sup> often in the presence of sodium chloride. The tungstates of the alkali metals and of magnesium are soluble in water, those of other metals being insoluble, or only slightly soluble, not only in water but also in dilute acids. Concentrated mineral acids (except phosphoric acid) decompose them, with separation of tungstic acid. In this reaction the paratungstates behave similarly, whereas the metatungstates are not decomposed.

Solutions of tungstates containing ammonium sulphide yield with hydrochloric acid a brown precipitate of tungsten trisulphide. The addition of zinc chloride to a tungstate solution produces a yellow precipitate which becomes blue on warming with dilute hydrochloric or sulphuric acid. When excess of hydrochloric acid is added to a solution of alkali tungstate and the mixture reduced by means of zinc, brilliant colours, from red to blue, are produced; <sup>3</sup> if phosphoric acid is used, a fine blue precipitate results.

The **paratungstates** are generally obtained by treating solutions of alkali normal tungstates with acid, or by double decomposition. They can only be obtained from solutions, and always contain water which appears essential to their constitution; it can only be removed with difficulty, strong heating being necessary for complete dehydration, which is accompanied by decomposition of the salt into the soluble normal salt and the insoluble tetratungstate. From an investigation <sup>4</sup> of the dehydration of the sodium and potassium salts the following results were obtained:

Temperature, t° C.	Water remaining after heating at t° C.	
	Na <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·28H <sub>2</sub> O.	K <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·11H <sub>2</sub> O.
110	5·0 molecules	5·4 molecules
150	4·0     ,,	4·4     ,,
200	2·4     ,,	2·4     ,,
250	1·4     ,,	1·4     ,,

The content of base to acid in paratungstates was first given by Laurent <sup>5</sup> as  $5R_2O : 12WO_3$ , whilst Lotz <sup>6</sup> and Scheibler <sup>7</sup> suggested

<sup>1</sup> Smith, *J. Amer. Chem. Soc.*, 1922, 44, 2027.

<sup>2</sup> Manross, *Annalen*, 1852, 81, 243; Geuther and Forsberg, *ibid.*, 1861, 120, 270; *Bull. Soc. chim.*, 1862, 4, 165; Schultze, *Annalen*, 1863, 126, 56.

<sup>3</sup> Mallet, *Trans. Chem. Soc.*, 1875, 23, 1228.

<sup>4</sup> Copaux, *Compt. rend.*, 1913, 156, 1771.

<sup>5</sup> Laurent, *loc. cit.*

<sup>6</sup> Lotz, *Annalen*, 1854, 91, 49; *Ann. Chim. Phys.*, 1855, [3], 43, 246.

<sup>7</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.



the formula  $3R_2O \cdot 7WO_3 \cdot xH_2O$ . Marignac,<sup>1</sup> after careful analysis, concluded that most paratungstates contained  $5R_2O : 12WO_3$ , but that a few contained  $3R_2O : 7WO_3$ . Other investigators,<sup>2</sup> for reasons mentioned above, were unable to decide between the two formulæ. Copaux, from the behaviour of the salts towards dehydration, considered them to be hydrotungstates and gave them the co-ordinative formula  $R'_5[H(W_2O_7)_3].aq.$  In support of this he points to the fact that the paratungstates resemble the complex tungstates in absorbing ultra-violet light, whereas normal tungstates do not do so. Rosenheim<sup>3</sup> suggests that they are 6-tungsto-aquates of composition  $R_5H_5[H_2(WO_4)_6].aq.$

Such formulation suggests a closer relation to the metatungstates than appears to be justified, and would not account for the very essential differences between the two types of compounds.

Paratungstates gradually decompose in aqueous solution with formation of the normal and metatungstates, so that while a freshly prepared solution is neutral to phenolphthalein, it gradually becomes acid on standing—more rapidly on boiling.<sup>4</sup> For this reason the electrical conductivities of the solutions slowly increase at ordinary temperatures.<sup>5</sup>

According to Hallopeau<sup>6</sup> the free paratungstic acid is formed in dilute solution when the barium salt is treated with dilute sulphuric acid. Concentration of the solution, even *in vacuo*, causes decomposition, and on prolonged boiling, metatungstic acid is formed. Alkalies neutralise the solution, yielding paratungstates. There is, however, no proof that this solution contains any special modification of tungstic acid.

In the following pages a description is given of the individual normal and acid salts of tungstic acid, including the paratungstates.

**Aluminium Tungstates.**—The *normal* salt,  $Al_2(WO_4)_3 \cdot 8H_2O$ , or  $Al_2O_3 \cdot 3WO_3 \cdot 8H_2O$ , is obtained<sup>7</sup> as a voluminous white precipitate when solutions of alum and normal sodium tungstate are mixed.<sup>8</sup> It is slightly soluble in water (1 in 1500). Sodium ditungstate with a concentrated solution of alum yields the *acid* salt,  $Al_2O_3 \cdot 4WO_3 \cdot 9H_2O$ , soluble in 400 parts of water at 15° C. Another acid salt,  $Al_2O_3 \cdot 5WO_3 \cdot 6H_2O$ , is formed by the addition of aluminium acetate to sodium tritungstate.<sup>9</sup> It is soluble in water, but is obtained as a white precipitate, which thickens to the consistency of honey, by the addition of alcohol.

*Aluminium paratungstate*,  $Al_2O_3 \cdot 7WO_3 \cdot 9H_2O$ , is obtained by precipitating a solution of ammonium paratungstate with an aluminium salt.<sup>10</sup>

By boiling a mixture of aluminium hydroxide and aqueous

<sup>1</sup> Marignac, *Ann. Chim. Phys.*, 1863, [3], 69, 5; *Compt. rend.*, 1862, 55, 888.

<sup>2</sup> von Knorre, *Ber.*, 1886, 19, 821; Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>3</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>4</sup> von Knorre, *Ber.*, 1885, 18, 2362.

<sup>5</sup> Wells, *J. Amer. Chem. Soc.*, 1907, 29, 112.

<sup>6</sup> Hallopeau, *Compt. rend.*, 1895, 121, 61; *Ann. Chim. Phys.*, 1900, [7], 19, 135.

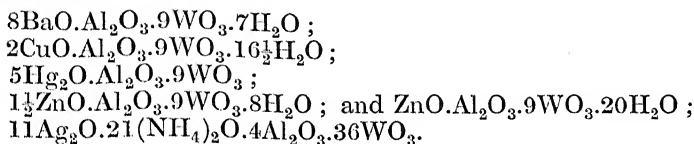
<sup>7</sup> Lefort, *Compt. rend.*, 1878, 87, 748; *Ann. Chim. Phys.*, 1878, [5], 15, 321; Anthon, *J. prakt. Chem.*, 1836, 9, 341.

<sup>8</sup> See also Bernoulli, *Pogg. Annalen*, 1860, 111, 576.

<sup>9</sup> Lefort, *Compt. rend.*, 1879, 88, 798; *Ann. Chim. Phys.*, 1879, [5], 17, 470.

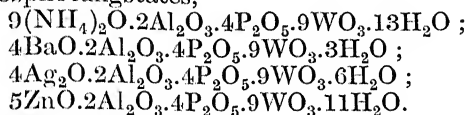
<sup>10</sup> Lotz, *Annalen*, 1854, 91, 49.

ammonium paratungstate, a complex salt, ammonium aluminotungstate,  $3(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , is obtained <sup>1</sup> as a highly refractive syrup which on drying leaves a semi-transparent mass. Other aluminotungstates containing the same ratio,  $\text{Al}_2\text{O}_3 : 9\text{WO}_3$ , have also been prepared, <sup>2</sup> viz. :

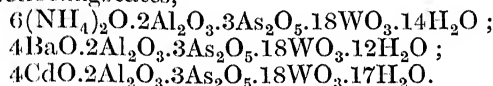


The following complex tungstates containing aluminium have been described : <sup>2</sup>

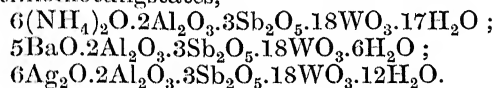
Alumino-phosphotungstates,



Alumino-arsenotungstates,



Alumino-antimoniotungstates,



**Ammonium Tungstates.**—The *normal* salt cannot be obtained by dissolving tungstic acid in aqueous ammonia, since on concentration ammonia is lost and an acid salt remains. That the normal tungstate is present in solution would appear evident from the fact that calcium chloride precipitates the normal calcium tungstate. It may be obtained as a white mass by the addition of hydrated tungstic acid to liquid ammonia.<sup>3</sup> The normal tungstate is very soluble in water and readily loses ammonia.

The *acid* tungstate,  $2(\text{NH}_4)_2\text{O} \cdot 3\text{WO}_3 \cdot 3\text{H}_2\text{O}$ , sometimes crystallises from a very concentrated neutral solution of tungstic acid in ammonia, which, however, more often yields the paratungstate.<sup>4</sup> The crystals, which are warty and indistinct, give off ammonia in contact with the air, leaving the paratungstate.

*Ammonium paratungstate*,  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$ , is the product most frequently obtained by the interaction of tungstic acid and ammonia; for example, when tungstic acid is dissolved in aqueous ammonia, or when ammonia is added to a solution of ammonium metatungstate, on concentration of the resulting solution the paratungstate crystallises out. It is dimorphous<sup>5</sup> and yields both acicular needles and laminated plates. The former are the more stable and are pseudo-

<sup>1</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1903, 25, 1229.

<sup>2</sup> Daniels, *ibid.*, 1908, 30, 1846.

<sup>3</sup> Rosenheim and Jacobsohn, *Zeitsch. anorg. Chem.*, 1906, 50, 297.

<sup>4</sup> Marignac, *Compt. rend.*, 1862, 55, 888; *Ann. Chim. Phys.*, 1863, [3], 69, 5.

<sup>5</sup> Laurent, *Ann. Chim. Phys.*, 1847, [3], 21, 54; *Comp. rend.*, 1847, 25, 538.

rhombic ( $a : b : c = 0.7995 : 1 : 0.4582$ ).<sup>1</sup> The plates are triclinic pinacoidal,  $a : b : c = 0.9785 : 1 : 1.2154$ ;  $\alpha = 65^\circ 47'$ ,  $\beta = 117^\circ 33'$ ,  $\gamma = 119^\circ 2'$ .<sup>2</sup> Both forms are stable at ordinary temperatures, but when heated, begin to lose ammonia at  $60^\circ \text{C.}$ ; at  $100^\circ \text{C.}$  lose 7 molecules of water;<sup>3</sup> and at  $250^\circ \text{C.}$  yield the glass-like colloidal tungstate (see below). If the crystals are heated in contact with dry ammonia, they lose water and absorb ammonia.<sup>4</sup> When boiled in aqueous solution for several days, the *metatungstate* is formed.

This salt was regarded by Berzelius and Anthon as the ditungstate; Lotz and Scheibler formulated it as  $3(\text{NH}_4)_2\text{O} \cdot 7\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , but the formula given above is due to Marignac. Rosenheim<sup>5</sup> suggests  $(\text{NH}_4)_{10}\text{H}_4[\text{H}_4(\text{WO}_4)_6(\text{W}_2\text{O}_7)_3] \cdot 7\text{H}_2\text{O}$ .

The *hydrate*,  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$  or  $3(\text{NH}_4)_2\text{O} \cdot 7\text{WO}_3 \cdot 3\text{H}_2\text{O}$ , is obtained by evaporation of a solution of ammonium paratungstate at temperatures near the boiling-point.<sup>6</sup> It yields small, glistening, monoclinic prisms,

$$a : b : c = 1.0442 : 1 : 0.7871; \beta = 109^\circ 50'.$$

On heating at  $100^\circ \text{C.}$  it loses 2 molecules of water. The electrical conductivity of solutions of this salt has been investigated.<sup>7</sup> At  $25^\circ \text{C.}$  the equivalent conductivity of a N/128 solution increased from 95.1 to 109.0 reciprocal ohms in six days. The rate of increase was greater when the temperature was raised and was complete in about three hours at  $80^\circ \text{C.}$  The following table shows the equivalent conductivities at  $25^\circ \text{C.}$  of solutions containing  $\frac{1}{10}$  of a molecular weight in  $v$  litres, (a) when freshly made, (b) after heating at  $80^\circ \text{C.}$  for three hours and then allowing to cool :

$v =$	32	64	128	256	512	1024
(a) $\Lambda =$	62.0	71.7	83.7	93.3	103.9	120.2
(b) $\Lambda =$	102	112	121	131	139	148.

A *hydrate*,  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , has been obtained<sup>8</sup> by the addition of acetic acid to a solution of ammonium tungstate.

The *acid salt*,  $2(\text{NH}_4)_2\text{O} \cdot 5\text{WO}_3 \cdot 5\text{H}_2\text{O}$ , is produced by cooling a hot saturated solution of ammonium paratungstate, when it separates<sup>9</sup> in small octahedral plates with crystallographic elements : <sup>10</sup>

$$a : b : c = 1.1204 : 1 : 1.7190; \alpha = 105^\circ 46', \beta = 95^\circ 17', \gamma = 90^\circ 1'.$$

It dissolves in 26 to 29 parts of water. On heating at  $100^\circ \text{C.}$  it loses about seven-tenths of its water of crystallisation.

The *octatungstate*,  $3(\text{NH}_4)_2\text{O} \cdot 8\text{WO}_3 \cdot 8\text{H}_2\text{O}$ , is sometimes obtained when a solution of the preceding salt is allowed to crystallise;<sup>11</sup> but

<sup>1</sup> Kerndt, *J. prakt. Chem.*, 1847, 41, 190; Schabus, *Best. d. Kristallgestalten*, Wien, 1855; Groth, *Chemische Kristallographie*, 1908, ii., 615.

<sup>2</sup> Marignac, *Compt. rend.*, 1862, 55, 888; *Ann. Chim. Phys.*, 1863, [3] 69, 5.

<sup>3</sup> Lotz, *Annalen*, 1854, 91, 49; Marignac, *loc. cit.*; Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139; Taylor (*J. Amer. Chem. Soc.*, 1902, 24, 629) gives loss at  $100^\circ \text{C.}$  of 6 mols.  $\text{H}_2\text{O}$ .

<sup>4</sup> Taylor, *loc. cit.*

<sup>5</sup> Rosenheim, *loc. cit.*

<sup>6</sup> Marignac, *loc. cit.*; Lotz, *loc. cit.*; Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273; Taylor, *loc. cit.*

<sup>7</sup> Wells, *J. Amer. Chem. Soc.*, 1907, 29, 112.

<sup>8</sup> Gibbs, *Amer. Chem. J.*, 1880, 1, 1, 217.

<sup>9</sup> Marignac, *loc. cit.*

<sup>10</sup> Groth, *Chemische Kristallographie*, 1908, ii., 611.

<sup>11</sup> Marignac, *loc. cit.*; Laurent, *Compt. rend.*, 1847, 25, 538; *Ann. Chim. Phys.*, 1847, [3], 21, 54.

from a hot solution, the trihydrate,  $2(\text{NH}_4)_2\text{O} \cdot 5\text{WO}_3 \cdot 3\text{H}_2\text{O}$ , has been obtained.<sup>1</sup>

A *colloidal* tungstate, of composition  $(\text{NH}_4)_2\text{O} \cdot 6\text{WO}_3 \cdot 4$  or  $6\text{H}_2\text{O}$ , results as a vitreous mass when ammonium para- or meta-tungstate is heated to  $250^\circ \text{C}$ .<sup>2</sup> It is miscible with water in all proportions and absorbs ammonia readily, thus reverting to the meta-salt.

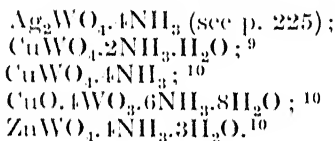
The following double *ammonium sodium tungstates* have been prepared:  $3(\text{NH}_4)_2\text{O} \cdot 3\text{Na}_2\text{O} \cdot 16\text{WO}_3 \cdot 22\text{H}_2\text{O}$ ; <sup>3</sup>  $16(\text{NH}_4)_2\text{O} \cdot 4\text{Na}_2\text{O} \cdot 50\text{WO}_3 \cdot 50\text{H}_2\text{O}$ ; <sup>4</sup>  $6(\text{NH}_4)_2\text{O} \cdot 5\text{Na}_2\text{O} \cdot 24\text{WO}_3 \cdot 27\text{H}_2\text{O}$ .<sup>5</sup>

The compound,  $\text{WO}_3 \cdot 3\text{NH}_3$ , probably *ammonium imidotungstate*,  $\text{NH} : \text{WO}(\text{O} \cdot \text{NH}_4)_2$ , is obtained <sup>6</sup> by heating the oxychloride,  $\text{WO}_2\text{Cl}_2$ , with liquid ammonia under pressure.

A tungstate of *hydroxylamine*,  $4\text{NH}_2\text{OH} \cdot 3\text{WO}_3 \cdot 3\text{H}_2\text{O}$ , is produced when hydroxylamine hydrochloride is added to a solution of sodium tungstate; it appears as a white precipitate which turns pale yellow on drying.<sup>7</sup>

*Hydroxylamine ammonium tungstate*,  $\text{NH}_4\text{O} \cdot \text{WO}_4 \cdot \text{NH}_4$ , is prepared <sup>8</sup> by treating finely powdered sodium paratungstate with an aqueous solution of hydroxylamine hydrochloride, and then dissolving the product in 15 per cent. ammonia. It crystallises in black tablets on evaporating the solution over potassium hydroxide. It is a strong reducer, and immediately reduces ammoniacal silver nitrate and Fehling's solution.

The following *ammonio-tungstates* have been described:



**Antimony Tungstates.**<sup>11</sup> The *normal* salt appears to be formed on mixing solutions of normal sodium tungstate and tartar-emetic as a white precipitate which is decomposed by washing with water. The *acid* salt,  $\text{Sb}_2\text{O}_3 \cdot 5\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , is formed as a yellow precipitate on mixing solutions of sodium ditungstate and tartar-emetic in presence of alcohol; it dissolves readily in water without decomposition. Another acid salt,  $\text{Sb}_2\text{O}_3 \cdot 6\text{WO}_3 \cdot 8\text{H}_2\text{O}$ , is obtained as a white precipitate by treating a solution of sodium tritungstate in a similar manner.

**Barium Tungstates.** The anhydrous *normal* salt,  $\text{BaWO}_4$ , may be obtained <sup>12</sup> by fusing together sodium tungstate, sodium chloride, and barium chloride. It crystallises in colourless octahedra = tetragonal

<sup>1</sup> Pinagel, *Dissertation*, Berne, 1904.

<sup>2</sup> Taylor, *J. Amer. Chem. Soc.*, 1902, **24**, 629.

<sup>3</sup> Hallopeau, *Ann. Chim. Phys.*, 1900, [7], **19**, 96.

<sup>4</sup> Gibbs, *Amer. Chem. J.*, 1880, **1**, 1, 217.

<sup>5</sup> Gibbs, *ibid.*, 1895, **17**, 181.

<sup>6</sup> Rosenheim and Jacobsen, *Zeitsch. anorg. Chem.*, 1906, **50**, 297.

<sup>7</sup> Allen and Gottschalk, *Amer. Chem. J.*, 1902, **27**, 328.

<sup>8</sup> Hofmann and Kölschütter, *Zeitsch. anorg. Chem.*, 1898, **16**, 463.

<sup>9</sup> Schiff, *Annalen*, 1862, **123**, 39.

<sup>10</sup> Briggs, *Trans. Chem. Soc.*, 1904, **85**, 672.

<sup>11</sup> Lefort, *Compt. rend.*, 1879, **88**, 798; *Ann. Chim. Phys.*, 1879, [5], **17**, 470.

<sup>12</sup> Geuther and Forsberg, *Annalen*, 1861, **120**, 270; Zettnow, *Pogg. Annalen*, 1867, **130**, 16, 241.

bipyramidal;  $a : c = 1 : 1.6046$ ,<sup>1</sup> of density, according to Zambonini,<sup>2</sup> 6.35. It is only slightly soluble in water. On heating, it first fuses and at high temperatures glows brightly.<sup>3</sup>

Various *hydrates* have been described. When a solution of barium metatungstate or metatungstic acid is treated with barium hydroxide solution a white gelatinous precipitate is formed which slowly becomes crystalline. According to Péchard,<sup>4</sup> the gelatinous precipitate has the composition  $\text{BaWO}_4 \cdot 2\text{H}_2\text{O}$ , whilst the crystalline precipitate is  $\text{BaWO}_4 \cdot \text{H}_2\text{O}$ . A precipitate, of composition  $\text{BaWO}_4 \cdot 2.5\text{H}_2\text{O}$ , is obtained<sup>5</sup> by adding barium chloride to a solution of sodium paratungstate containing acetic acid. If barium hydroxide solution is added to a boiling solution of sodium paratungstate until the precipitate no longer redissolves, and the liquid is then allowed to cool, a double salt of sodium and barium (see below) separates; on adding excess of barium hydroxide solution to the mother-liquor a white crystalline precipitate of the pure subhydrated normal tungstate,  $2\text{BaWO}_4 \cdot \text{H}_2\text{O}$ , is obtained.<sup>6</sup>

Barium tungstate has been recommended for use instead of white lead<sup>7</sup> and for colouring porcelain.<sup>8</sup>

*Barium ditungstate*,  $\text{BaO} \cdot 2\text{WO}_3 \cdot \text{H}_2\text{O}$ , is obtained according to Lefort<sup>9</sup> by double decomposition from solutions of sodium ditungstate and barium acetate, as a white amorphous precipitate, slightly soluble in water. The existence of this compound has been disputed.<sup>10</sup>

*Barium paratungstate*,  $3\text{BaO} \cdot 7\text{WO}_3 \cdot x\text{H}_2\text{O}$ , is precipitated on adding excess of a barium salt to a solution of an alkali paratungstate. When dried in the air the salt contains  $16\text{H}_2\text{O}$ ; dried over sulphuric acid,  $8\text{H}_2\text{O}$ ; dried at  $100^\circ \text{C}$ .,  $4\text{H}_2\text{O}$ .<sup>11</sup> The *double salt*,  $3\text{Na}_2\text{O} \cdot 2\text{BaO} \cdot 12\text{WO}_3 \cdot 24\text{H}_2\text{O}$ , or  $2\text{Na}_2\text{O} \cdot \text{BaO} \cdot 7\text{WO}_3 \cdot 14\text{H}_2\text{O}$ , separates when excess of barium hydroxide solution is added to a boiling solution of sodium paratungstate and the mixture is allowed to cool.<sup>6</sup>

The *acid salt*,  $4\text{BaO} \cdot 10\text{WO}_3 \cdot 22\text{H}_2\text{O}$ , is obtained as a white insoluble granular powder when barium chloride is added to a boiling aqueous solution of the corresponding sodium salt.<sup>12</sup>

*Barium tritungstate*,  $\text{BaO} \cdot 3\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , is obtained as a white amorphous precipitate by the addition of cold water to barium metatungstate;<sup>6</sup> a similar precipitate is obtained on mixing solutions of barium acetate and sodium tritungstate,<sup>13</sup> which on drying at  $100^\circ \text{C}$ . gives a product of composition  $\text{BaO} \cdot 3\text{WO}_3 \cdot 4\text{H}_2\text{O}$ . It dissolves in 300 parts of water at  $15^\circ \text{C}$ . Boiling water decomposes it with formation of the insoluble ditungstate and the soluble metatungstate.

An *acid tungstate*, of composition  $\text{BaO} \cdot 8\text{WO}_3 \cdot 8\text{H}_2\text{O}$ , is described by

<sup>1</sup> Groth, *Chemische Krystallographie*, 1908, ii., 395.

<sup>2</sup> Zambonini, *Zeitsch. Kryst. Min.*, 1895, 41, 53; but Clarke and Davis (*Amer. J. Sci.*, 1877, [3], 14, 281) give a density of 5.00 at  $13.5^\circ \text{C}$ . and 5.04 at  $15^\circ \text{C}$ .

<sup>3</sup> Weiss, Martin, and Stimmelmayer, *Zeitsch. anorg. Chem.*, 1910, 65, 279.

<sup>4</sup> Péchard, *Compt. rend.*, 1889, 108, 1167.

<sup>5</sup> Zettnow, *Pogg. Annalen*, 1867, 130, 16, 241. See also Anthon, *J. prakt. Chem.*, 1836, 9, 341; Lefort, *Ann. Chim. Phys.*, 1878, [5], 15, 321; Smith and Bradbury, *Ber.*, 1892, 24, 2930; *Bull. Soc. chim.*, 1891, [3], 8, 279.

<sup>6</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>7</sup> Schoen, *J. Soc. Chem. Ind.*, 1900, 19, 740; Sacc, *Compt. rend.*, 1869, 68, 315.

<sup>8</sup> Granger, *Compt. rend.*, 1893, 116, 106.

<sup>9</sup> Lefort, *loc. cit.*

<sup>10</sup> Kantschew, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 729.

<sup>11</sup> Lotz, *Annalen*, 1854, 91, 49; von Knorre, *Ber.*, 1885, 18, 326, 2362.

<sup>12</sup> Smith, *J. Amer. Chem. Soc.*, 1922, 44, 2027.

<sup>13</sup> Lefort, *Ann. Chim. Phys.*, 1879, [5], 17, 470.

Zettnow,<sup>1</sup> who obtained it by the addition of hydrochloric acid and barium chloride to a solution of sodium paratungstate which contained sufficient phosphoric acid to prevent precipitation by hydrochloric acid alone; according to Scheibler the precipitate so formed is not of definite composition.

Complex **beryllium tungstates** corresponding with the formulæ:  $x\text{BeCl}_2.y\text{BeWO}_4.z\text{BeO}$  and  $x\text{Be}(\text{NO}_3)_2.y\text{BeWO}_4.z\text{BeO}$ , have been prepared.<sup>2</sup>

**Normal Bismuth Tungstate**,  $\text{Bi}_2(\text{WO}_4)_3$ , is dimorphous,<sup>3</sup> crystallising in (1) the monoclinic system,

$$a : b : c = 1.006 : 1 : 1.520, \beta = 90^\circ 34',$$

and (2) the tetragonal system,

$$a : c = 1 : 1.566.$$

The monoclinic crystals have density 8.24 at  $7.5^\circ \text{C.}$  and melt at  $832^\circ \text{C.}$ <sup>4</sup>

The bismuth salt,  $\text{Bi}_2\text{O}_3.6\text{WO}_3.8\text{H}_2\text{O}$ ,<sup>5</sup> is obtained as a white precipitate on mixing solutions of bismuth acetate and sodium tritungstate in presence of alcohol.

**Cadmium Tungstates.**—The anhydrous *normal* salt,  $\text{CdWO}_4$ , remains as colourless crystals when a mixture containing sodium tungstate (4 parts), sodium chloride (16 parts), and cadmium chloride (11 parts) is heated to complete fusion and allowed to cool.<sup>6</sup> The *hydrate*,  $\text{CdWO}_4.2\text{H}_2\text{O}$ , is formed by double decomposition.<sup>7</sup>

*Cadmium paratungstate*,  $3\text{CdO}.7\text{WO}_3.16\text{H}_2\text{O}$ , is obtained, according to Gonzalez,<sup>8</sup> as a white crystalline precipitate on mixing hot solutions of an alkali paratungstate and a cadmium salt. The crystals are infusible and become orange coloured after heating. Lotz,<sup>9</sup> using ammonium paratungstate, obtained the *double* salt,  $12\text{CdO}.3(\text{NH}_4)_2\text{O}.35\text{WO}_3.35\text{H}_2\text{O}$ , whilst from solutions containing molecular proportions of sodium paratungstate and cadmium sulphate at  $80^\circ \text{C.}$  von Knorre<sup>10</sup> obtained white crystals of composition  $2\text{CdO}. \text{Na}_2\text{O}.7\text{WO}_3.18\text{H}_2\text{O}$ .

The *tritungstate*,  $\text{CdO}.3\text{WO}_3.4\text{H}_2\text{O}$ , is obtained as a white translucent gummy mass by mixing solutions of cadmium acetate and sodium tritungstate, and drying at  $100^\circ \text{C.}$ <sup>5</sup>

**Calcium Tungstates.**—The *normal* tungstate,  $\text{CaWO}_4$ , occurs native as *scheelite* (see p. 182). It may be obtained by fusing together sodium tungstate and anhydrous calcium chloride, either with or without the addition of common salt;<sup>11</sup> the resulting crystals are similar in form to scheelite, that is, tetragonal bipyramidal,  $a : c = 1 : 1.5356$ ,

<sup>1</sup> Zettnow, *loc. cit.*

<sup>2</sup> Tanata and Kurowski, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 813.

<sup>3</sup> Zambonini, *Gazzetta*, 1920, 50, ii., 128.

<sup>4</sup> The system  $\text{Bi}_2(\text{WO}_4)_3 - \text{PbWO}_4$  has been investigated thermally by Zambonini, *loc. cit.*

<sup>5</sup> Lefort, *Compt. rend.*, 1878, 87, 748; 1879, 88, 798.

<sup>6</sup> Geuther and Forsberg, *Annalen*, 1861, 120, 270; Zettnow, *loc. cit.*

<sup>7</sup> Anthon, *loc. cit.*; Smith and Bradbury, *loc. cit.*

<sup>8</sup> Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>9</sup> Lotz, *Annalen*, 1854, 91, 49.

<sup>10</sup> von Knorre, *Ber.*, 1886, 19, 819.

<sup>11</sup> Manross, *Annalen*, 1852, 81, 243; Michel, *Bull. Soc. min. de France*, 1879, 2, 142.

and of density 6.06 to 6.08.<sup>1</sup> The amorphous form is readily obtained by mixing solutions of a calcium salt and sodium tungstate. The precipitated calcium tungstate is converted to the crystalline variety by fusion with sodium chloride,<sup>2</sup> or by heating with lime in a current of hydrogen chloride.<sup>3</sup> This salt is used for preparing the phosphorescent screens used in experiments with Röntgen rays.

*Calcium ditungstate* in the anhydrous state was supposed by Lefort to result from the double decomposition of sodium ditungstate and calcium acetate, whilst concentration of the mother-liquor yielded crystals presumed to be the trihydrate. However, the existence of these compounds is not established<sup>4</sup> since the products obtained vary in composition.

*Calcium paratungstate*,  $3\text{CaO} \cdot 7\text{WO}_3 \cdot 18\text{H}_2\text{O}$ , is prepared in a similar manner to the corresponding barium salt. The salt sometimes contains  $19\text{H}_2\text{O}$ . It is more soluble than the barium and strontium paratungstates,<sup>5</sup> and may be heated to redness without melting. The *double salt*,  $3\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 12\text{WO}_3 \cdot 34\text{H}_2\text{O}$ , is obtained<sup>6</sup> by adding lime-water or a solution of a calcium salt in excess to a boiling solution of sodium paratungstate, and allowing to cool. White crystals separate, which, when heated, fuse, and on cooling set to a black mass.

The salt,  $4\text{CaO} \cdot 10\text{WO}_3 \cdot 25\text{H}_2\text{O}$ , is obtained in a similar manner to the corresponding barium salt.<sup>7</sup> It is a white, infusible, granular powder.

*Calcium tritungstate*,  $\text{CaO} \cdot 3\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , is obtained by mixing concentrated solutions of sodium tritungstate and calcium acetate, or calcium chloride (Lefort). The precipitate is decomposed by hot water into the di- and meta-tungstates.

**Cerium Tungstate**,<sup>8</sup>  $\text{Ce}_2(\text{WO}_4)_3$ , is obtained by mixing solutions of cerium sulphate and sodium tungstate and igniting the pale yellow precipitate produced. It yields crystals of density 6.514 at  $12^\circ \text{C}$ ., with specific heat 0.0821<sup>9</sup> and melting-point  $1089^\circ \text{C}$ .<sup>10</sup> It is also formed by adding cerium dioxide to fused sodium paratungstate<sup>11</sup> and remains after washing with water.

The *double tungstate*,  $4\text{Na}_2\text{O} \cdot \text{Ce}_2\text{O}_3 \cdot 7\text{WO}_3$  or  $\text{Na}_3\text{Ce}_2(\text{WO}_4)_7$ , has been prepared<sup>12</sup> by dissolving a mixture of cerium dioxide and tungsten trioxide in a fused mixture of sodium chloride and sodium tungstate, excess of the latter being present. An *ammonium ceritungstate*,  $2(\text{NH}_4)_2\text{O} \cdot \text{Ce}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , is obtained as a red transparent glass<sup>13</sup> insoluble in water, when cerium hydroxide is boiled for eight hours with a solution of ammonium paratungstate, the mixture filtered, and the filtrate evaporated to dryness.

Yellow and red crystalline *chlorotungstates* have been produced by fusion of sodium tungstate and cerium chloride mixtures;<sup>11</sup> and by the action of hydrogen chloride on tungsten and cerium dioxides.

<sup>1</sup> Manross, *Annalen*, 1852, 81, 243; Zambonini, *Gazzetta*, 1920, 50, ii., 128.

<sup>2</sup> Cossa, *Ber.*, 1879, 12, 683.

<sup>3</sup> Debray, *Compt. rend.*, 1862, 55, 287.

<sup>4</sup> Kantschew, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 729.

<sup>5</sup> von Knorre, *Ber.*, 1885, 18, 326.

<sup>6</sup> Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>7</sup> Smith, *J. Amer. Chem. Soc.*, 1922, 44, 2027.

<sup>8</sup> For a general account of the rare earth tungstates, see this series, Vol. IV., p. 265

<sup>9</sup> Cossa and Zecchini, *Gazzetta*, 1880, 10, 225; *Ber.*, 1880, 13, 1861.

<sup>10</sup> Zambonini, *Atti R. Accad. Lincei*, 1913, [5], 22, i., 519.

<sup>11</sup> Didier, *Compt. rend.*, 1886, 102, 823.

<sup>12</sup> Högbom, *Bull. Soc. chim.*, 1884, 42, 2.

<sup>13</sup> Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, 26, 1474.

**Chromium Tungstates.**—The *paratungstate*,  $\text{Cr}_2\text{O}_3 \cdot 7\text{WO}_3 \cdot \text{H}_2\text{O}$ , is prepared by mixing solutions of ammonium paratungstate and chromic chloride, and drying at  $100^\circ \text{C}$ . the resulting greyish-green precipitate;<sup>1</sup> or by treating a cold solution of sodium paratungstate with *violet* chromic chloride.<sup>2</sup> The green chromic chloride produces a basic salt. The following compounds have been described:  $\text{Cr}_2\text{O}_3 \cdot 5\text{WO}_3$ ,<sup>3</sup>  $\text{Cr}_2\text{O}_3 \cdot 5\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3 \cdot 4\text{WO}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3 \cdot 3\text{WO}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3 \cdot 2\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ,<sup>4</sup> but these appear to be either identical with the paratungstate, or mixtures of the para- and meta-salts.<sup>5</sup>

**Cobalt Tungstates.**—The anhydrous *normal* salt,  $\text{CoWO}_4$ , is obtained as greenish-black crystals by fusing together sodium tungstate, sodium chloride, and cobalt chloride.<sup>6</sup> The hydrate,  $\text{CoWO}_4 \cdot 2\text{H}_2\text{O}$ , results as a violet precipitate when a solution of alkali tungstate is treated with a solution of a cobalt salt.<sup>7</sup>

*Cobalt ditungstate*,  $\text{CoO} \cdot 2\text{WO}_3 \cdot 3\text{H}_2\text{O}$ ,<sup>7</sup> is obtained as a reddish-brown precipitate by double decomposition.

*Cobalt paratungstate*,  $3\text{CoO} \cdot 7\text{WO}_3 \cdot 25\text{H}_2\text{O}$ , is formed as a bright rose-coloured microcrystalline precipitate on mixing solutions of sodium paratungstate and a cobalt salt.<sup>8</sup> It does not melt at a red heat, but on cooling it acquires a bluish tinge. The *double* salt,  $3\text{Na}_2\text{O} \cdot 2\text{CoO} \cdot 12\text{WO}_3 \cdot 30\text{H}_2\text{O}$ , is prepared in the same way as the corresponding double salt of calcium. It forms rose-coloured crystals which melt at red heat and solidify, on cooling, to a black lustrous mass. Double salts, of composition  $2\text{Na}_2\text{O} \cdot 3\text{CoO} \cdot 12\text{WO}_3 \cdot 41\text{H}_2\text{O}$  and  $\text{Na}_2\text{O} \cdot 4\text{CoO} \cdot 12\text{WO}_3 \cdot 23\text{H}_2\text{O}$ , have been prepared by Rosenheim,<sup>9</sup> who suggests for them the formulæ  $\text{Na}_4\text{Co}_3\text{H}_{10}[\text{H}_2(\text{WO}_4)_6]_2 \cdot 34\text{H}_2\text{O}$  and  $\text{NaCo}_2\text{H}_5[\text{H}_2(\text{WO}_4)_6] \cdot 16\text{H}_2\text{O}$ , respectively.

The salt,  $4\text{CoO} \cdot 10\text{WO}_3 \cdot 35\text{H}_2\text{O}$ , is obtained as a pink granular powder by the method used for the corresponding barium salt.<sup>10</sup>

*Cobalt tritungstate*,  $\text{CoO} \cdot 3\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , is described by Lefort.

*Lutecocobaltic fluoroxytungstate*,  $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 2\text{WO}_2\text{F}_2$  (see p. 194).

**Copper Tungstates.**—*Basic* copper tungstates are found native as *cuprotungstite*, while the mineral *cuproscheelite* contains a copper calcium tungstate (see p. 182). By fusing together sodium tungstate, sodium chloride, and cupric chloride, light green octahedral crystals are obtained which probably consist of basic copper tungstate.<sup>11</sup> The *normal* cupric tungstate,  $\text{CuWO}_4 \cdot 2\text{H}_2\text{O}$ , is precipitated by the addition of a cupric salt to a normal tungstate solution. It is a light green powder which becomes brownish on heating, with loss of water, and finally melts, yielding a crystalline mass on cooling. It is insoluble in water, but soluble in ammonia, phosphoric acid, or acetic acid.<sup>7</sup>

*Cupric ditungstate*,  $\text{CuO} \cdot 2\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , is stated by Anthon to be

<sup>1</sup> Lotz, *Annalen*, 1854, 91, 49.

<sup>2</sup> Kantschew, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 729.

<sup>3</sup> Smith, *J. Amer. Chem. Soc.*, 1893, 15, 151; Smith and Dieck, *Zeitsch. anorg. Chem.*, 1894, 5, 13.

<sup>4</sup> Lefort, *Compt. rend.*, 1878, 87, 748; 1879, 88, 798.

<sup>5</sup> Kantschew, *loc. cit.*; Lotz, *Ann. Chim. Phys.*, 1855, [3], 43, 246; *Annalen*, 1854, 91, 49.

<sup>6</sup> Schultze, *Annalen*, 1863, 126, 56; Zettnow, *Pogg. Annalen*, 1867, 130, 16, 241.

<sup>7</sup> Anthon, *J. prakt. Chem.*, 1836, 9, 341.

<sup>8</sup> Gonzalez, *loc. cit.*

<sup>9</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>10</sup> Smith, *loc. cit.*

<sup>11</sup> Schultze, *loc. cit.*



formed as a light green precipitate when a cupric salt is added to a ditungstate solution, but the actual composition of such precipitates is doubtful.

A *cuprous cupric tungstate*, of composition  $\text{Cu}_2\text{WO}_4 \cdot 2\text{CuWO}_4$ , results as a reddish-brown crystalline powder after lixiviation of the melt obtained by fusing together copper sulphate and sodium tungstate in molecular proportions,<sup>1</sup> or a mixture containing sodium tungstate (2 parts), sodium chloride (1 part), and cuprous chloride (3 parts).<sup>2</sup>

*Copper paratungstate*,  $3\text{CuO} \cdot 7\text{WO}_3 \cdot 19\text{H}_2\text{O}$  or  $5\text{CuO} \cdot 12\text{WO}_3 \cdot 33\text{H}_2\text{O}$ , is formed as a light blue or bluish-green microcrystalline precipitate on the addition of excess of copper sulphate to a solution of sodium paratungstate at  $70^\circ \text{C}$ .<sup>3</sup> The salt after heating becomes yellow. It is insoluble in water. When equimolecular proportions of the two salts are used, greenish crystals of the double salt,  $3\text{Na}_2\text{O} \cdot 3\text{CuO} \cdot 14\text{WO}_3 \cdot 32\text{H}_2\text{O}$ , are obtained. If excess of the copper salt is added to a boiling solution of sodium paratungstate, slender bright blue needles of composition  $4\text{Na}_2\text{O} \cdot \text{CuO} \cdot 12\text{WO}_3 \cdot 32\text{H}_2\text{O}$  separate. Rosenheim<sup>4</sup> obtained from a cold mixture of the solutions, a light blue crystalline powder to which he gives the formula  $\text{Na}_3\text{CuH}_5[\text{H}_2(\text{WO}_4)_6]11 \cdot 5\text{H}_2\text{O}$ .

*Copper ammonio-tungstates* (see p. 213).

**Erbium** yields the *double tungstate*,  $3\text{Na}_2\text{O} \cdot 2\text{Er}_2\text{O}_3 \cdot 9\text{WO}_3$  or  $\text{Na}_6\text{Er}_4(\text{WO}_4)_9$ ,<sup>5</sup> when the oxide is mixed with tungstic acid and dissolved in a fused mixture of sodium chloride and sodium tungstate, excess of the former being present.

**Gadolinium** yields a double tungstate similar in composition to the cerium compound.

**Indium Tungstate**,  $\text{In}_2(\text{WO}_4)_3 \cdot 8\text{H}_2\text{O}$ , is obtained by double decomposition.<sup>6</sup>

**Iron Tungstates.**—*Ferrous tungstate* occurs in the minerals *ferberite* and *reinite* (see p. 181) and with manganese in *wolframite*. It may be prepared in the crystalline form by fusing together sodium tungstate, sodium chloride, and ferrous chloride; the crystals, which are lustrous, black, and opaque, have density 7.1.<sup>7</sup> It is also formed when a mixture of tungstic anhydride and ferrous oxide is strongly heated in a current of hydrogen chloride.<sup>8</sup> The *trihydrate*,  $\text{FeWO}_4 \cdot 3\text{H}_2\text{O}$ , is precipitated as a light brown powder by the addition of a ferrous salt to sodium tungstate solution.<sup>9</sup>

*Ferrous ditungstate*,  $\text{FeO} \cdot 2\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , results as a cinnamon-brown precipitate when a ferrous salt is added to a solution of sodium ditungstate.

*Ferric Tungstate.*—The cream-coloured precipitate formed on the addition of a ferric salt to a solution of ammonium tungstate is considered by Lotz<sup>10</sup> to be ferric tungstate. The salts,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{WO}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3 \cdot 2\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3 \cdot 4\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , are described by Lefort.

<sup>1</sup> Zettnow, *Pogg. Annalen*, 1867, **130**, 16, 241.

<sup>2</sup> Schultze, *Annalen*, 1863, **126**, 56.

<sup>3</sup> von Knorre, *Ber.*, 1886, **19**, 819; Gonzalez, *J. prakt. Chem.*, 1887, [2], **36**, 44.

<sup>4</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, **96**, 139.

<sup>5</sup> Högbon, *Bull. Soc. chim.*, 1884, **44**, 2.

<sup>6</sup> Renz, *Dissertation*, Breslau, 1902; *Ber.*, 1901, **34**, 2763.

<sup>7</sup> Geuther and Forsberg, *Annalen*, 1861, **120**, 270.

<sup>8</sup> Debray, *Compt. rend.*, 1862, **55**, 287.

<sup>9</sup> Anthon, *J. prakt. Chem.*, 1836, **9**, 341.

<sup>10</sup> Lotz, *Annalen*, 1854, **91**, 49.

A complex *ferritungstic acid* and corresponding salts have been isolated,<sup>1</sup> the acid being considered by Rosenheim to be a tetrabasic ferrihexatungstic acid of composition  $H_9[Fe(WO_4)_6]$ , the ammonium and potassium salts having the formula  $R_4H_5[Fe(WO_4)_6].9H_2O$ . The latter are precipitated by adding the alkali chloride to a mixture of the alkali paratungstate and ferric chloride. A guanidinium salt,  $(CH_6N_3)_3H_6[Fe(WO_4)_6].5H_2O$ , has also been prepared.

**Lanthanum Tungstate.**—A solution of sodium tungstate yields with lanthanum chloride, in presence of alcohol, a precipitate which on drying has a pale blue colour.<sup>2</sup> By dissolving lanthanum oxide and tungstic acid in fused sodium tungstate, the *double tungstate*,  $4Na_2O.La_2O_3.7WO_3$  or  $Na_8La_2(WO_4)_7$ , may be obtained after washing with water in which it is insoluble;<sup>3</sup> if excess of sodium chloride is present in the melt, the salt obtained is  $3Na_2O.2La_2O_3.9WO_3$ . The following lanthanitungstates have been prepared:<sup>4</sup>  $2(NH_4)_2O.La_2O_3.16WO_3.16H_2O$ ,  $5BaO.La_2O_3.16WO_3.16H_2O$ , and  $5Ag_2O.La_2O_3.16WO_3.16H_2O$ ; these are white amorphous powders, insoluble in water.

**Lead Tungstates.**—The *normal salt* occurs native as *stolzite* and *raspite* (see p. 182). It may be obtained, by the addition of a lead salt to a solution of an alkali tungstate,<sup>5</sup> as a white flocculent precipitate slightly soluble in water. On heating, it melts at  $1130^\circ C$ .<sup>6</sup> and forms crystals on cooling. Octahedral crystals of lead tungstate are prepared by fusing together sodium tungstate and lead chloride<sup>7</sup> or lead sulphate.<sup>8</sup> The crystals are transparent, of density 8.24, insoluble in water and nitric acid, but soluble in alkalis.

*Lead paratungstate*,  $3PbO.7WO_3.10H_2O$ , is obtained as a white precipitate on adding a solution of lead nitrate to a solution of ammonium paratungstate.<sup>9</sup> The *double salt*,  $4Na_2O.PbO.12WO_3.28H_2O$ , corresponding to the copper salt described above, yields slender white needles.<sup>10</sup>

*Lead tritungstate* is described by Lefort.

**Lithium Tungstates.**—The *normal salt*,  $Li_2WO_4$ , is formed in solution when a suspension of tungstic anhydride in water is boiled with lithium carbonate,<sup>11</sup> or when tungstic anhydride is added to fused lithium carbonate and the resulting mass extracted with water;<sup>12</sup> on evaporation, short, thick, oblique rhombic prisms separate, which readily dissolve in water yielding an alkaline solution. Lithium ditungstate is described by Anthon, but its existence is doubtful.

*Lithium paratungstate*,  $5Li_2O.12WO_3.33H_2O$  or  $3Li_2O.7WO_3.19H_2O$ , is prepared by adding tungstic acid to a solution of lithium carbonate

<sup>1</sup> Laurent, *Compt. rend.*, 1850, 31, 392, 693; Rosenheim and Schwer, *Zeitsch. anorg. Chem.*, 1914, 89, 224.

<sup>2</sup> Hitchcock, *J. Amer. Chem. Soc.*, 1895, 17, 483, 520.

<sup>3</sup> Högbom, *loc. cit.*

<sup>4</sup> Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, 26, 1474.

<sup>5</sup> Anthon, *loc. cit.*; Zettnow, *Pogg. Annalen*, 1867, 130, 240; Smith and Bradbury, *Ber.*, 1891, 24, 2930.

<sup>6</sup> Zambonini, *Gazzetta*, 1920, 50, ii., 128.

<sup>7</sup> Manross, *Annalen*, 1852, 81, 243; 82, 348.

<sup>8</sup> Michel, *Thesis*, Paris, 1889.

<sup>9</sup> Lotz, *J. prakt. Chem.*, 1854, 63, 214; Smith and Bradbury, *Bull. Soc. chim.*, 1892, [3], 8, 280.

<sup>10</sup> Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>11</sup> Gmelin, *Handbook of Chemistry*, 1850, iv., 42.

<sup>12</sup> Anthon, *loc. cit.*

until the mixture is neutral to litmus, and allowing the product to evaporate slowly over sulphuric acid. It crystallises in orthorhombic tables or prisms, which are stable in air<sup>1</sup> and are more soluble in water than the corresponding sodium and potassium salts. When heated to a high temperature in a current of hydrogen it is reduced to tungsten dioxide (see p. 199).

*Lithium tetratungstate*,  $\text{Li}_2\text{O} \cdot 4\text{WO}_3$ , remains as needle-shaped crystals<sup>2</sup> after well washing with water the mass obtained by fusing together lithium carbonate (5 molecules) and tungstic anhydride (12 molecules).

**Magnesium Tungstates.**—*Normal magnesium tungstate*,  $\text{MgWO}_4$ , is formed by fusion of sodium tungstate with sodium and magnesium chlorides,<sup>3</sup> and remains after washing out the more soluble salts as lustrous orthorhombic crystals<sup>4</sup> isomorphous with the calcium salt. The *trihydrate*,  $\text{MgWO}_4 \cdot 3\text{H}_2\text{O}$ , was obtained by Lefort<sup>5</sup> by mixing solutions of sodium tungstate and magnesium acetate in presence of alcohol; the precipitate was readily soluble in water. The *heptahydrate*,  $\text{MgWO}_4 \cdot 7\text{H}_2\text{O}$ , is obtained by boiling tungstic acid with magnesium carbonate in suspension in water; a clear solution results, which, on cooling, deposits glistening prisms<sup>6</sup> which readily dissolve in hot water.

*Magnesium ditungstate*,  $\text{MgO} \cdot 2\text{WO}_3 \cdot 8\text{H}_2\text{O}$ , was prepared by Lefort by heating a suspension of magnesium hydroxide with excess of tungstic acid, and allowing the solution formed to crystallise; rhomboidal prisms separate, which are readily soluble in water.

*Magnesium paratungstate*,  $3\text{MgO} \cdot 7\text{WO}_3 \cdot 24\text{H}_2\text{O}$ , is obtained as white crystals by mixing warm solutions of alkali paratungstate and magnesium sulphate, the latter in excess.<sup>7</sup> The salt is slightly soluble in cold water, more so in hot, and is easily decomposed by acids. If molecular proportions of sodium paratungstate and magnesium sulphate are mixed in solution at 70° C., the double salt,  $3\text{Na}_2\text{O} \cdot 0.3\text{MgO} \cdot 1.4\text{WO}_3 \cdot 33\text{H}_2\text{O}$ , is produced. Similar double salts containing ammonium,  $2(\text{NH}_4)_2\text{O} \cdot 3\text{MgO} \cdot 12\text{WO}_3 \cdot 24\text{H}_2\text{O}$ <sup>8</sup> and  $(\text{NH}_4)_2\text{O} \cdot 2\text{MgO} \cdot 7\text{WO}_3 \cdot 10\text{H}_2\text{O}$ ,<sup>9</sup> have been prepared. It is probable that these two salts are identical.

*Magnesium tritungstate*,  $\text{MgO} \cdot 3\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , results as a white precipitate<sup>5</sup> on the addition of alcohol to a mixture of sodium tritungstate and magnesium acetate solutions; it is soluble in water.

**Manganese Tungstates.**—The anhydrous *normal* salt,  $\text{MnWO}_4$ , occurs in the mineral *hübnerite* (see p. 181) and with ferrous tungstate in *wolframite*. It may be prepared by the method used for the normal magnesium salt,<sup>3</sup> and yields light brown, highly lustrous, rhombic crystals, transparent<sup>10</sup> and of density 6.7. The *dihydrate*,  $\text{MnWO}_4 \cdot 2\text{H}_2\text{O}$ , is precipitated from solutions of manganous salts by the addition of sodium tungstate as a greyish-white powder which becomes anhydrous on heating.

*Manganese paratungstate*,  $3\text{MnO} \cdot 7\text{WO}_3 \cdot 20\text{H}_2\text{O}$  or  $5\text{MnO} \cdot 12\text{WO}_3$ .

<sup>1</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>2</sup> von Knorre, *ibid.*, 1883, [2], 27, 49.

<sup>3</sup> Geuther and Forsberg, *Annalen*, 1861, 120, 270.

<sup>4</sup> Michel, *Bull. Soc. min. de France*, 1879, 2, 142.

<sup>5</sup> Lefort, *Compt. rend.*, 1878, 87, 748; 1879, 88, 798.

<sup>6</sup> Ullik, *J. prakt. Chem.*, 1868, 103, 147; *Bull. Soc. chim.*, 1869, 11, 50.

<sup>7</sup> von Knorre, *Ber.*, 1886, 19, 819.

<sup>8</sup> Marignac, *Compt. rend.*, 1862, 55, 888.

<sup>9</sup> Lotz, *J. prakt. Chem.* 1854, 63, 214.

<sup>10</sup> Groth and Arzruni, *Pogg. Annalen*, 1873, 149, 236.

$34\text{H}_2\text{O}$ , is formed as an amorphous white precipitate on adding a solution of a manganous salt to sodium paratungstate.<sup>1</sup> The salt is soluble in dilute hydrochloric acid. It becomes yellowish green after ignition. By mixing solutions of sodium paratungstate and manganese sulphate in molecular proportions at  $70^\circ\text{C}$ .<sup>2</sup> the pale yellow crystalline *double salt*,  $3\text{Na}_2\text{O} \cdot 3\text{MnO} \cdot 14\text{WO}_3 \cdot 36\text{H}_2\text{O}$ , is obtained, whilst with potassium paratungstate the double salt,  $3\text{K}_2\text{O} \cdot 2\text{MnO} \cdot 12\text{WO}_3 \cdot 16\text{H}_2\text{O}$ , results<sup>3</sup> as small yellow prismatic crystals which are slightly soluble in water and lose  $10\text{H}_2\text{O}$  on heating at  $100^\circ\text{C}$ . By boiling ammonium paratungstate and manganic hydroxide with water, large red octahedral crystals, of composition  $4(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 12\text{WO}_3 \cdot 23\text{H}_2\text{O}$ , are obtained<sup>4</sup> on evaporation.

The salt,  $4\text{MnO} \cdot 10\text{WO}_3 \cdot 30\text{H}_2\text{O}$ , is prepared by the method described for the corresponding barium salt (see p. 214). It is a colourless granular powder.<sup>5</sup>

*Manganese tritungstate*,  $\text{MnO} \cdot 3\text{WO}_3 \cdot 5\text{H}_2\text{O}$ , is obtained by double decomposition in presence of alcohol.<sup>6</sup>

A complex tungstate, of composition  $3\text{Na}_2\text{O} \cdot 5\text{WO}_3 \cdot \text{MnO}_2 \cdot 18\text{H}_2\text{O}$  or  $\text{Na}_6\text{H}_2[\text{MnO}(\text{WO}_4)_5] \cdot 17\text{H}_2\text{O}$ ,<sup>7</sup> has been prepared<sup>8</sup> by the action of excess of sodium tungstate on manganese sulphate in presence of ammonium persulphate; reddish-brown crystals separate which are easily decomposed by water.

**Mercury Tungstates.**—*Normal mercurous tungstate*,  $\text{Hg}_2\text{WO}_4$ , is formed,<sup>9</sup> on adding a soluble mercurous salt to a solution of alkali tungstate, as a yellow precipitate, which darkens in colour when dried and leaves tungstic anhydride when ignited. Owing to its insolubility in water, this salt affords a means for the separation and estimation of tungstic acid (see p. 270). An acid mercurous salt,  $2\text{Hg}_2\text{O} \cdot 3\text{WO}_3 \cdot 8\text{H}_2\text{O}$ , is described by Lefort, but its existence is doubtful.

*Normal mercuric tungstate*,  $\text{HgWO}_4$ , is obtained as a light yellow precipitate on adding the acetate to a saturated solution of sodium tungstate.<sup>6</sup> A *basic salt*,  $3\text{HgO} \cdot 2\text{WO}_3$ , is obtained as a heavy white precipitate when a boiling solution of mercuric chloride is treated with an insufficient quantity of alkali tungstate.<sup>9</sup> An *acid salt*,  $2\text{HgO} \cdot 3\text{WO}_3$ , is formed as a white precipitate on mixing neutral solutions of mercuric nitrate and an alkali tungstate. Both these salts are insoluble in water, are decomposed by boiling alkalies with separation of mercuric oxide, and on ignition yield tungstic anhydride.

The following salts have been described: <sup>6</sup>  $\text{HgO} \cdot 3\text{WO}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{HgO} \cdot 5\text{WO}_3 \cdot 5\text{H}_2\text{O}$ , and  $3\text{HgO} \cdot 5\text{WO}_3 \cdot 5\text{H}_2\text{O}$ .

**Neodymium Tungstate** is formed as a gelatinous precipitate on the addition of neodymium chloride to a solution of sodium tungstate.<sup>10</sup>

<sup>1</sup> Anthon, *J. prakt. Chem.*, 1836, 9, 341; Lotz, *Annalen*, 1854, 91, 49; Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>2</sup> von Knorre, *loc. cit.*

<sup>3</sup> Hallopeau, *Compt. rend.*, 1898, 127, 621, 755; *Bull. Soc. chim.*, 1898, [3], 19, 955, 977.

<sup>4</sup> Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, 26, 1474.

<sup>5</sup> Smith, *ibid.*, 1922, 44, 2027.

<sup>6</sup> Lefort, *loc. cit.*

<sup>7</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139; Rosenheim and Schwer, *ibid.*, 1914, 89, 233.

<sup>8</sup> Just, *Ber.*, 1903, 36, 3619.

<sup>9</sup> Anthon, *loc. cit.*

<sup>10</sup> Hitchcock, *J. Amer. Chem. Soc.*, 1895, 17, 483, 520.

Its colour, a very pale rose, changes on ignition to lavender. Its solubility in water decreases as the temperature rises.

*Complex neodymytungstates*, of composition  $3(\text{NH}_4)_2\text{O} \cdot \text{Nd}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 20\text{H}_2\text{O}$  and  $6\text{BaO} \cdot \text{Nd}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 17\text{H}_2\text{O}$ , have been prepared.<sup>1</sup>

**Nickel Tungstates.**—The anhydrous normal salt is obtained in well-defined, brown, lustrous, translucent, rhombic prisms, of density 6.88,<sup>2</sup> by fusing together sodium tungstate, sodium chloride, and nickel chloride.<sup>3</sup> The *hydrates*,  $\text{NiWO}_4 \cdot 3\text{H}_2\text{O}$ <sup>4</sup> and  $\text{NiWO}_4 \cdot 6\text{H}_2\text{O}$ ,<sup>5</sup> are obtained by precipitation as light green powders which yield the anhydrous salt on heating.

The *acid tungstates*,  $\text{NiO} \cdot 2\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{NiO} \cdot 2\text{WO}_3 \cdot 7\text{H}_2\text{O}$ , and  $\text{NiO} \cdot 3\text{WO}_3 \cdot 4\text{H}_2\text{O}$ , are described by Lefort.

*Nickel paratungstate*,  $3\text{NiO} \cdot 7\text{WO}_3 \cdot 14\text{H}_2\text{O}$ , is obtained as a light green precipitate when solutions of a nickel salt and an acid tungstate of sodium are mixed.<sup>6</sup>

The salt,  $4\text{NiO} \cdot 10\text{WO}_3 \cdot 34\text{H}_2\text{O}$ , obtained in a similar manner to the barium salt (see p. 214), is a greenish-white powder.

By the addition of a nickel salt to a large excess of alkali paratungstate, Rosenheim has prepared well-defined crystalline salts, corresponding to the ferri-tungstates (see p. 219), for which he suggests the formulæ:  $\text{Na}_3\text{H}_7[\text{Ni}(\text{WO}_4)_6] \cdot 18\text{H}_2\text{O}$ , or  $\text{Na}_3\text{NiH}_5[\text{H}_2(\text{WO}_4)_6] \cdot 18\text{H}_2\text{O}$ , and  $(\text{NH}_4)_3\text{H}_7[\text{Ni}(\text{WO}_4)_6] \cdot 7.5\text{H}_2\text{O}$ , or  $(\text{NH}_4)_3\text{NiH}_5[\text{H}_2(\text{WO}_4)_6] \cdot 7.5\text{H}_2\text{O}$ .<sup>7</sup>

Complex salts containing trivalent nickel, and of composition  $3(\text{NH}_4)_2\text{O} \cdot \text{Ni}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 22\text{H}_2\text{O}$  and  $2(\text{NH}_4)_2\text{O} \cdot \text{Ni}_2\text{O}_3 \cdot 8\text{WO}_3 \cdot 14\text{H}_2\text{O}$ , are obtained by boiling hydrated nickel dioxide with an ammoniacal ammonium paratungstate solution.<sup>1</sup>

**Platinum Tungstates.**—Only complex salts are known. When platonic hydroxide is boiled with a solution of an alkali tungstate, yellow needle-shaped crystals separate which show the reactions of a paratungstate.<sup>8</sup> The composition of the product is  $5\text{Na}_2\text{O} \cdot 2\text{PtO}_2 \cdot 7\text{WO}_3 \cdot 35\text{H}_2\text{O}$ , but it cannot be recrystallised and is probably a double salt of sodium paratungstate and sodium platinate,  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 + 2(\text{Na}_2\text{O} \cdot \text{PtO}_2) \cdot 35\text{H}_2\text{O}$ . By using paratungstates of the alkali metals, Gibbs<sup>9</sup> obtained a series of crystalline products which appeared to be complex platino-tungstates. According to Rosenheim, however, they were alkali paratungstates containing occluded platonic hydroxide.

**Potassium Tungstates.**—The anhydrous *normal salt*,  $\text{K}_2\text{WO}_4$ , is prepared by fusing together equivalent quantities of tungstic anhydride and potassium hydroxide or potassium carbonate,<sup>10</sup> the resulting mass being taken up with water and allowed to crystallise; or by boiling a solution of potassium hydroxide or carbonate in presence of tungstic acid.<sup>11</sup> Thin, needle-shaped, monoclinic prisms, with axial ratio,

$$a : b : c = 1.9702 : 1 : 1.2341; \text{ and } \beta = 113^\circ 15',^{12}$$

<sup>1</sup> Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, 26, 1474.

<sup>2</sup> Clarke and Davis, *Amer. J. Sci.*, 1877, [3], 14, 281. <sup>3</sup> Schultze, *Annalen*, 1863, 126, 56.

<sup>4</sup> Lefort, *Compt. rend.* 1878, 87, 748; 1879, 88, 798.

<sup>5</sup> Anthon, *J. prakt. Chem.*, 1836, 9, 341.

<sup>6</sup> Anthon, *loc. cit.*; Lotz, *Annalen*, 1854, 91, 49.

<sup>7</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>8</sup> Rosenheim, *Ber.*, 1891, 24, 2397.

<sup>9</sup> Gibbs, *ibid.*, 1877, 10, 1384; *Amer. J. Sci.*, 1877, [3], 14, 62; *Amer. Chem. J.*, 1895, 17, 73.

<sup>10</sup> Anthon, *loc. cit.*; Zettnow, *Pogg. Annalen*, 1867, 130, 240; Ullik, *J. prakt. Chem.*, 1868, 103, 147; *Bull. Soc. chim.*, 1869, 11, 50.

<sup>11</sup> Marignac, *Compt. rend.*, 1862, 55, 888; *Ann. Chim. Phys.*, 1863, [3], 69, 5; Anthon, *loc. cit.* See also Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 49.

<sup>12</sup> Marignac, *loc. cit.*

and isomorphous with potassium manganate and potassium molybdate,<sup>1</sup> are obtained, which are readily soluble in water, decrepitate when heated, and melt at about 921° to 926° C.<sup>2</sup> The salt, however, appears to be dimorphous, laminated crystals often accompanying the prisms.<sup>3</sup>

The *dihydrate*,  $K_2WO_4 \cdot 2H_2O$ , crystallises when the solution is concentrated over sulphuric acid at temperatures below 10° C. in lustrous monoclinic prisms and tables, with axial ratio

$$a : b : c = 0.9998 : 1 : 0.7830; \text{ and } \beta = 110^\circ 57'.$$

The crystals effloresce in dry air, but are deliquescent in moist air. Other hydrates have been described, for example,  $K_2WO_4 \cdot H_2O$ , slender needles,<sup>4</sup> which was probably partly dehydrated dihydrate; and  $K_2WO_4 \cdot 5H_2O$ , hexagonal prisms,<sup>5</sup> which according to Ullik<sup>6</sup> was a sodium-potassium tungstate.

The solution of normal potassium tungstate is strongly alkaline in reaction; its density at various concentrations at 15° C. has been determined<sup>7</sup> as follows:

Concentration (per cent.)	2.42	6.57	8.72	16.19
Density	1.0202	1.0575	1.0781	1.1548

Various *acid* tungstates have been described. The compound formulated as the ditungstate,  $K_2O \cdot 2WO_3 \cdot 3H_2O$ , in earlier literature<sup>8</sup> has been shown to be the paratungstate.

*Potassium paratungstate*,  $5K_2O \cdot 12WO_3 \cdot 11H_2O$  or  $3K_2O \cdot 7WO_3 \cdot 6H_2O$ , is prepared by the action of acid on the normal tungstate; for example, (i) by saturating a solution with carbon dioxide,<sup>9</sup> (ii) by adding acetic acid to a cold concentrated solution and boiling the resulting white precipitate with water,<sup>10</sup> or (iii) by boiling the solution with a solution of tungstic acid.<sup>11</sup> It may also be obtained by fusing together tungstic anhydride with potassium carbonate or potassium tungstate, and lixiviating the fused mass. The salt is deposited from solution as a crystalline powder consisting of iridescent scales. Electrolysis of a solution of the normal tungstate in a cell in which the electrodes are separated by a diaphragm<sup>12</sup> also yields the paratungstate.

The crystals are triclinic pinacoids,

$$a : b : c = 0.9137 : 1 : 1.1362; \alpha = 65^\circ 36', \beta = 117^\circ 22', \gamma = 115^\circ 39',$$

<sup>1</sup> Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 6.

<sup>2</sup> Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215; van Klooster, *ibid.*, 1914, 85, 49. Amadori (*Atti R. Accad. Lincei*, 1913, [5], 22, i., 609) gives melting-point 894° C. The density and molecular surface energy of the molten salt have been determined at various temperatures by Jaeger, see *Zeitsch. anorg. Chem.*, 1917, 101, 183, 188; Jaeger and Kahn, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 381. The curves of crystallisation of the systems,  $K_2SO_4$ — $K_2WO_4$ ,  $K_2CrO_4$ — $K_2WO_4$ , and  $K_2MoO_4$ — $K_2WO_4$ , have been investigated by Amadori, *loc. cit.*

<sup>3</sup> Marignac, *loc. cit.*

<sup>4</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5.

<sup>5</sup> Anthon, *loc. cit.*

<sup>6</sup> Ullik, *loc. cit.*

<sup>7</sup> Traube, *Zeitsch. anorg. Chem.*, 1895, 8, 12. Vapour-pressure determinations are given by Tammann, *Mém. de l'Acad. Pétersbourg*, 1887, [7], 35.

<sup>8</sup> Anthon, *loc. cit.*; Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 49; Lefort, *ibid.*, 1876, [5], 9, 93; *Compt. rend.*, 1876, 82, 1182.

<sup>9</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5; Marignac, *ibid.*, 1863, [3], 69, 5.

<sup>10</sup> Lefort, *ibid.*, 1876, [5], 9, 93; 1878, [5], 15, 321; 1879, [3], 17, 470; von Knorre, *J. prakt. Chem.*, 1883, [2], 27, 49.

<sup>11</sup> Anthon, *loc. cit.*; Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>12</sup> Schaefer, *Zeitsch. anorg. Chem.*, 1904, 38, 174.

and are isomorphous with ammonium paratungstate.<sup>1</sup> The salt is somewhat soluble in cold water and dissolves readily in hot. Solubility data by Anthon, Riche, and Marignae are not in agreement. According to the last named, 1 part of the salt dissolves in 71 parts of water at 20° C., but when a saturated solution is prepared by boiling the salt with water for several days the cooled solution at 18° C. contains 1 part of the salt

after	1 day dissolved in	5.62 parts of water		
„	26 days	„	11.9	„
„	153	„	15.6	„
„	334	„	15.6	„

It is insoluble in alcohol. When heated it loses water, and at a red heat fuses, undergoing decomposition,<sup>2</sup> and on cooling sets to a yellow crystalline mass.

Two other hydrates of potassium paratungstate,  $5K_2O.12WO_3.10H_2O$ <sup>3</sup> and  $5K_2O.12WO_3.14H_2O$ , or  $3K_2O.7WO_3.8H_2O$ ,<sup>4</sup> have been described.

The salt,  $2K_2O.5WO_3.4H_2O$ , is obtained as an amorphous precipitate by adding a cold concentrated solution of the normal salt to excess of glacial acetic acid;<sup>5</sup> it is soluble in 20 parts of water, and the solution on evaporation at ordinary temperatures deposits prismatic tables. The solution decomposes on boiling. This salt may also be produced by the addition of potassium chloride to a hot solution of sodium paratungstate, or by crystallisation from a hot solution of potassium paratungstate.<sup>6</sup>

*Potassium tritungstate*,  $K_2O.3WO_3.2H_2O$ , is obtained,<sup>5</sup> by pouring a concentrated solution of the normal salt into a boiling solution of acetic acid, as a white precipitate, which must be filtered immediately and washed with alcohol in order to prevent the formation of metatungstate. It dissolves in 5 to 6 parts of water, and the solution on concentration yields fine needle-shaped crystals or prisms; but on boiling or prolonged heating decomposition occurs.

The acid salts,  $5K_2O.14WO_3$  and  $K_2O.8WO_3$ , have also been described.<sup>7</sup>

The double tungstate,  $K_2Na_4(WO_4)_3.14H_2O$ , has been obtained by Ullik,<sup>8</sup> whilst Hallopeau<sup>9</sup> describes a tungstate of potassium and tungsten, of composition  $K_2O.WO_2.4WO_3$ , prepared by heating potassium paratungstate with tin for one hour at a temperature sufficiently high to melt the tungstate. On treating the residue successively with boiling water, concentrated hydrochloric acid, boiling potassium carbonate (50 per cent. solution), and finally hot water, the compound is obtained as dark blue prismatic crystals.

**Praseodymium Tungstate** is obtained<sup>10</sup> as a greenish-yellow

<sup>1</sup> Marignae, *Ann. Chim. Phys.*, 1863, [3], 69, 5.

<sup>2</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5; von Knorre, *J. prakt. Chem.*, 1883, [2], 27, 49.

<sup>3</sup> Gibbs, *Proc. Amer. Acad.*, 1880, 15, 1; *Amer. Chem. J.*, 1880, 1, 1, 217.

<sup>4</sup> Zettnow, *Pogg. Annalen*, 1867, 130, 16, 241.

<sup>5</sup> Lefort, *Compt. rend.*, 1876, 82, 1182; *Ann. Chim. Phys.*, 1876, [5], 9, 93.

<sup>6</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139. See also Gibbs, *Amer. Chem. J.*, 1880, 1, 1, 217.

<sup>7</sup> von Knorre, *loc. cit.*

<sup>8</sup> Ullik, *Sitzungsber. K. Akad. Wiss. Wien*, 1867, 56, 148.

<sup>9</sup> Hallopeau, *Bull. Soc. chim.*, 1899, [3], 21, 267.

<sup>10</sup> Hitchcock, *J. Amer. Chem. Soc.*, 1895, 17, 483, 520.

gelatinous precipitate when the chloride is added to a solution of sodium tungstate; unlike the corresponding neodymium salt (see p. 221), its solubility in water increases with rise in temperature.

By boiling praseodymium hydroxide with aqueous ammonium paratungstate and evaporating to dryness, the complex salt,  $2(\text{NH}_4)_2\text{O} \cdot \text{Pr}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 16\text{H}_2\text{O}$ , is obtained as a green transparent gum.<sup>1</sup> The corresponding barium and silver salts, having composition  $4\text{BaO} \cdot \text{Pr}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 7\text{H}_2\text{O}$ ,  $6\text{BaO} \cdot \text{Pr}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 9\text{H}_2\text{O}$ , and  $4\text{Ag}_2\text{O} \cdot \text{Pr}_2\text{O}_3 \cdot 16\text{WO}_3 \cdot 8\text{H}_2\text{O}$ , have also been prepared.

**Rubidium Tungstates.**—The *pentatungstate*,  $\text{Rb}_2\text{O} \cdot 5\text{WO}_3$ , prepared by fusing together rubidium oxide (1 part) and tungstic oxide (3 to 3.5 parts), yields glistening rectangular leaflets.<sup>2</sup> The *octatungstate*,  $\text{Rb}_2\text{O} \cdot 8\text{WO}_3$ , has also been obtained.

**Samarium Tungstate.**—A double salt of composition  $3\text{Na}_2\text{O} \cdot 2\text{Sm}_2\text{O}_3 \cdot 9\text{WO}_3$  has been prepared in the same way as the corresponding lanthanum compound (see p. 219).

**Silver Tungstates.**—The *normal* salt,  $\text{Ag}_2\text{WO}_4$ , is produced as a fine yellow precipitate when a solution of sodium tungstate is treated with silver nitrate;<sup>3</sup> it is slightly soluble in water and, on heating, turns dark purple and melts. A tungstate containing excess of silver and called “argentous” tungstate<sup>4</sup> has been shown to be a mixture of the normal salt and metallic silver.<sup>5</sup> An *ammoniotungstate*,  $\text{Ag}_2\text{WO}_4 \cdot 4\text{NH}_3$ , is formed when ammonia is added to a solution of a silver salt, or when the dry silver salt is saturated with ammonia gas;<sup>6</sup> in the former case, tabular crystals are obtained on evaporation; in the latter, a white bulky powder remains. It is soluble in water, but the solution decomposes. On heating, the substance loses all its ammonia at  $60^\circ \text{C}$ .

**Silver Paratungstate**,  $5\text{Ag}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$ , is obtained<sup>7</sup> as a whitish-yellow crystalline precipitate on adding a solution of a silver salt to a solution of sodium paratungstate. After drying at  $60^\circ \text{C}$ . it contains  $8\text{H}_2\text{O}$ . It melts at a red heat, and on cooling solidifies to a white lustrous crystalline mass.

**Sodium Tungstates.**—The anhydrous *normal* tungstate,  $\text{Na}_2\text{WO}_4$ , is prepared by the fusion method described for potassium tungstate (see p. 222), or by complete dehydration of the hydrates at  $100^\circ \text{C}$ . or over sulphuric acid.<sup>8</sup> It may be obtained from the mineral wolframite by fusion with alkali as already described (see p. 202).

The anhydrous salt exists as white crystals, of density 4.1833 at  $18.5^\circ \text{C}$ . and 4.1743 at  $20.5^\circ \text{C}$ .,<sup>9</sup> which melt at  $698^\circ \text{C}$ .<sup>10</sup> On heating it undergoes two transformations, the first with considerable development of heat, and finally boils. The transition temperatures between the polymorphic forms thus indicated have been determined from the cooling and heating curves as follows:

<sup>1</sup> Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, **26**, 1474.

<sup>2</sup> Schaefer, *Zeitsch. anorg. Chem.*, 1904, **38**, 142.

<sup>3</sup> Smith and Bradbury, *Ber.*, 1891, **24**, 2930; Zettnow, *loc. cit.*

<sup>4</sup> Wöhler and Rautenberg, *Annalen*, 1860, **114**, 119.

<sup>5</sup> Muthmann, *Ber.*, 1887, **20**, 983.

<sup>6</sup> Widmann, *Bull. Soc. chim.*, 1873, [2], **20**, 64.

<sup>7</sup> Gonzalez, *J. prakt. Chem.*, 1887, [2], **36**, 44.

<sup>8</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], **50**, 5; Foreher, *Sitzungsber. K. Akad. Wiss. Wien*, 1862, **44**, 164; Pawlewski, *Ber.*, 1900, **33**, 1223; Funk, *ibid.*, **33**, 3700.

<sup>9</sup> Clarke and Davis, *Amer. J. Sci.*, 1877, [3], **14**, 281.

<sup>10</sup> According to Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2027, melting-point =  $665^\circ \text{C}$ .

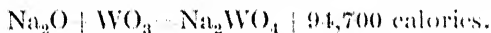


Method.	Transition Point.		Melting-point of $\beta$ Form.
	$\delta \rightleftharpoons \gamma$ ,*	$\gamma \rightleftharpoons \beta$ .	
Cooling curve 1	° C. 570	° C. ..	° C. 698
" 2	564	588	698
" 3	568	585	698
" 4	572	589	700
Heating curve 5	587	591	694

\* The designation of the different forms is due to Boeke,<sup>2</sup> and is chosen from the behaviour of the three salts in the binary systems  $\text{Na}_2\text{WO}_4 - \text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{WO}_4 - \text{Na}_2\text{MoO}_4$ , and the ternary system  $\text{Na}_2\text{WO}_4 - \text{Na}_2\text{MoO}_4 - \text{Na}_2\text{SO}_4$ .

The binary systems  $\text{Na}_2\text{WO}_4 - \text{Na}_2\text{SiO}_3$  and  $\text{Na}_2\text{WO}_4 - \text{K}_2\text{WO}_4$ , and the properties of aqueous solutions of the mixtures, have been investigated.<sup>6</sup>

The heat of formation of sodium tungstate has been found to be : 7



The aqueous solution, which is alkaline, when allowed to crystallise at temperatures above 6° C., yields slender nacreous crystals of the *dihydrate*,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , in the form of rhombic bipyramidal scales,  $a : b : c = 0.8002 : 1 : 0.6470$ ,<sup>8</sup> of density 3.259 at 17.5° C. and 3.231 at 19° C.<sup>9</sup> This hydrate is stable in the air, and it is in this form that the salt is generally used. When heated, it loses water at 200° C., becomes opaque, and finally melts. It dissolves readily in hot water, but may be precipitated by means of alcohol. The solution yields white tungstic acid on the addition of mineral acids.

If the aqueous solution is allowed to crystallise at temperatures below 6° C., the *decahydrate*,  $\text{Na}_2\text{WO}_4 \cdot 10\text{H}_2\text{O}$ , is obtained.<sup>10</sup>

The solubility of sodium tungstate has been determined by Funk<sup>11</sup> as follows :

Solid Phase $\text{Na}_2\text{WO}_4 \cdot 10\text{H}_2\text{O}$ .		Solid Phase $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ .	
Temperature, ° C.	Grams $\text{Na}_2\text{WO}_4$ in 100 Grams Solution.	Temperature, ° C.	Grams $\text{Na}_2\text{WO}_4$ in 100 Grams Solution.
—5	30.60	— 3.5	41.67
—4	31.87	+ 0.5	41.73
—3.5	32.98	+ 21	42.27
—2	34.52	+ 43.5	43.98
0	36.54	+ 80.5	47.65
+ 3	39.20	+ 100	49.31
+ 5	41.02		

<sup>1</sup> Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

<sup>2</sup> Boeke, *ibid.*, 1906, 50, 355.

<sup>3</sup> Parravano, *Gazzetta*, 1909, 39, ii., 55.

<sup>4</sup> van Klooster, *Zeitsch. anorg. Chem.*, 1911, 69, 135.

<sup>5</sup> van Klooster and Gerns, *ibid.*, 1914, 86, 369.

<sup>6</sup> van Liempt, *ibid.*, 1922, 122, 175. See also van Klooster, *ibid.*, 1910, 69, 135.

<sup>7</sup> Mixer, *Amer. J. Sci.*, 1908, [4], 26, 125.

<sup>8</sup> Marignac, *Compt. rend.*, 1862, 55, 888.

<sup>9</sup> Clarke and Davis, *Amer. J. Sci.*, 1877, [3], 14, 281.

<sup>10</sup> Funk, *Ber.*, 1900, 33, 3700.

<sup>11</sup> Funk, *loc. cit.* See also Anthon ; Riche, *Ann. Chim. Phys.*, 1857, [3], 59, 5.

These results are shown graphically in fig. 4.

The densities and refractive indices of solutions of various concentrations have been determined as follows : <sup>1</sup>

Grams $\text{Na}_2\text{WO}_4$ in 100 Grams Solution.	Density, $d_{40}^{20.0}$ .	Refractive Index, $n_D^{20.0}$ .
2.21	1.0184	1.33586
10.08	1.0949	1.34516
16.56	1.1667	1.35376
20.59	1.2148	1.35933
25.46	1.2789	1.36648
32.68	1.3854	1.37934
38.43	1.4828	1.38890

The equivalent conductivities of solutions containing  $\frac{1}{2}\text{Na}_2\text{WO}_4$  in  $v$  litres at  $25^\circ\text{C}$ . are as follows : <sup>2</sup>

$v = 32$	64	128	256	512	1024
$\Lambda = 95.9$	101.8	105.4	110.3	112.9	116.4. <sup>3</sup>

The vapour pressures of solutions have been determined.<sup>4</sup>

The production of colloidal tungsten hydroxide by the electrolysis

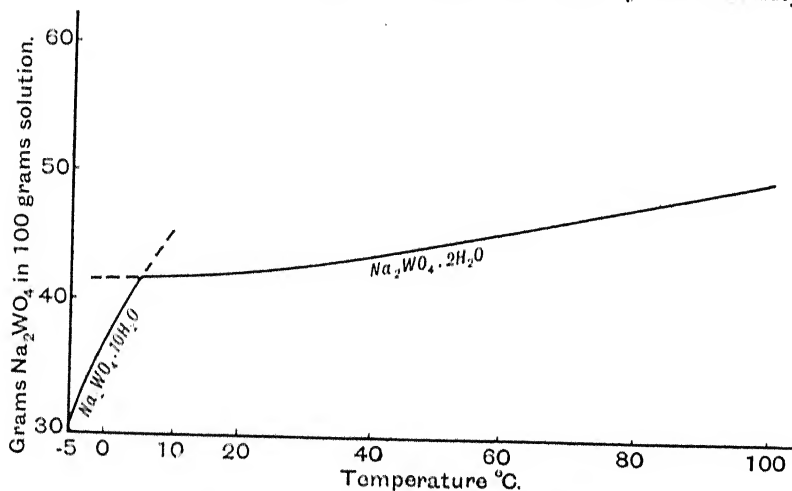


FIG. 4.—Solubility of sodium tungstate.

of a solution of sodium tungstate has already been<sup>5</sup> described (p. 207). If precautions are taken to prevent the sodium hydroxide formed at

<sup>1</sup> Pawlewski, *Ber.*, 1900, 33, 1223. See also Franz, *J. prakt. Chem.*, 1871, [2], 4, 238 ; 5, 282 ; Traube, *Zeitsch. anorg. Chem.*, 1895, 8, 12.

<sup>2</sup> Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

<sup>3</sup> For further data see Eitzbacher, *Dissertation*, Berlin, 1899 ; Grossmann and Krämer, *Zeitsch. anorg. Chem.*, 1904, 41, 43 ; Wells, *J. Amer. Chem. Soc.*, 1907, 29, 112 ; Watkins and Jones, *ibid.*, 1916, 37, 2626.

<sup>4</sup> Tammann, *Mém. de l'Acad. Pétersbourg*, 1887, [7], 35.

the cathode from reaching the anode, for example, by means of a porous partition, it is possible to prepare the paratungstate, or other complex tungstate, from the anode solution.<sup>1</sup>

The use of sodium tungstate has been recommended as a mordant, and it has been used as a fire-proofing material for flannelette, but owing to its solubility it cannot be considered satisfactory and it is not now used.

*Sodium ditungstate*,  $\text{Na}_2\text{O} \cdot 2\text{WO}_3$ , may be obtained by fusing together tungstic anhydride and sodium hydroxide or sodium carbonate, the mixture containing  $1\text{Na}_2\text{O} : 2\text{WO}_3$ .<sup>2</sup> On cooling, long needles separate, which on prolonged heating with water dissolve, yielding an alkaline solution which contains metatungstate. The *dihydrate*,  $\text{Na}_2\text{O} \cdot 2\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , is described by Rammelsberg<sup>3</sup> as a crystalline precipitate obtained by addition of hydrochloric acid to a solution of the normal tungstate. The *hexahydrate*,  $\text{Na}_2\text{O} \cdot 2\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , is stated by Lefort<sup>4</sup> to crystallise from a solution containing the normal tungstate (2 molecules) and acetic acid (1 molecule); von Knorre,<sup>2</sup> however, could only obtain the paratungstate from such a solution. The hydrate,  $\text{Na}_2\text{O} \cdot 2\text{WO}_3 \cdot 12\text{H}_2\text{O}$ , has also been described.<sup>5</sup>

*Sodium paratungstate* is known commercially as "tungstate of soda" and may be prepared on a large scale by fusing wolframite with soda ash and lixiviating the fused mass. On nearly neutralising the boiling solution with hydrochloric acid and allowing to crystallise, large triclinic crystals of the salt separate.

The salt may be formed in solution by any of the following methods :

1. Saturation of a solution of sodium hydroxide, carbonate, or tungstate, with anhydrous tungstic acid.<sup>6</sup>
2. Treatment of a sodium tungstate solution with hydrochloric acid at boiling-point (as described above) until only faintly alkaline to litmus.<sup>7</sup>
3. Addition of a solution of sodium metatungstate (containing 5.8 grams  $\text{Na}_2\text{O} \cdot 4\text{WO}_3 \cdot 10\text{H}_2\text{O}$ ) to one of the normal tungstate (containing 2 grams  $\text{Na}_2\text{O} \cdot \text{WO}_3 \cdot 2\text{H}_2\text{O}$ ).<sup>8</sup>
4. Saturation of a solution of normal sodium tungstate with carbon dioxide.<sup>9</sup>

5. Electrolysis of sodium tungstate solution in a cell in which the electrodes are separated by a diaphragm (see above).<sup>10</sup>

From the solutions so prepared various hydrates have been obtained and are described under many different formulæ. There appear, however, to be five distinct salts which show distinctive properties, varying from one another in degrees of solubility, crystalline form, etc.

- (i)  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$ <sup>11</sup> is formed when crystallisation takes

<sup>1</sup> Lottermoser, *Kolloid Zeitsch.*, 1922, 121, 243.

<sup>2</sup> von Knorre, *J. prakt. Chem.*, 1883, [2], 27, 49.

<sup>3</sup> Rammelsberg, *Pogg. Annalen*, 1855, 94, 514.

<sup>4</sup> Lefort, *Compt. rend.*, 1876, 82, 1182; *Ann. Chim. Phys.*, 1876, [5], 9, 93.

<sup>5</sup> Friedheim, *Ber.*, 1890, 23, 1509.

<sup>6</sup> Anthon, *J. prakt. Chem.*, 1836, 9, 341.

<sup>7</sup> Scheibler, *ibid.*, 1860, 80, 204; 1861, 83, 273; Gibbs, *Proc. Amer. Acad.*, 1880, 15, 1; *Amer. Chem. J.*, 1880, 1, 1, 217; von Knorre, *loc. cit.*; Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>8</sup> von Knorre, *Ber.*, 1885, 18, 326, 2362.

<sup>9</sup> Forcher, *Sitzungsber. K. Akad. Wiss. Wien*, 1862, 44, 164.

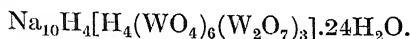
<sup>10</sup> Schaefer, *Zeitsch. anorg. Chem.*, 1904, 38, 174; Lottermoser, *loc. cit.*

<sup>11</sup> Formula due to Laurent and established by Marignac. This compound was formulated as  $\text{Na}_2\text{O} \cdot 2\text{WO}_3 \cdot 4\text{H}_2\text{O}$  by Anthon,  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 14\text{H}_2\text{O}$  by Lotz,  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$  by Scheibler, and  $2\text{Na}_2\text{O} \cdot 5\text{WO}_3 \cdot 12\text{H}_2\text{O}$  by Forcher.

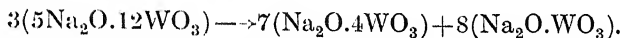
place at ordinary or lower temperatures. It yields transparent or milky triclinic pinacoidal crystals with

$$a : b : c = 0.5341 : 1 : 1.1148 ; \alpha = 93^\circ 56', \beta = 113^\circ 36', \gamma = 85^\circ 55',$$

of density 3.987 at 14° C. and stable in air. On heating, the salt loses, according to Scheibler, 10.42 per cent. of water—21 of the 28 molecules  $\text{H}_2\text{O}$  would correspond to a loss of 10.52 per cent. ; according to Rosenheim<sup>1</sup> the loss at 100° C. corresponds to  $24\text{H}_2\text{O}$ , and he therefore suggests the formula



The remaining water is lost at 300° C., and the residue, which has density 5.49, is still completely soluble in water. At a red heat—according to Smith<sup>2</sup> at 705.8° C.—the salt melts to a clear, yellowish, oily liquid and undergoes decomposition, for on cooling it sets to a crystalline mass which is only partly soluble in water, the insoluble residue being the tetratungstate,  $\text{Na}_2\text{O}.4\text{WO}_3$ . According to von Knorre<sup>3</sup> the decomposition may be represented thus :



Solubility data for sodium paratungstate have been given as follows :

One part of salt dissolves in 8<sup>4</sup> or 12<sup>5</sup> parts of cold water, or 12.6 parts of water at 22° C.<sup>6</sup>

If the salt is boiled for some time with water, a solution is obtained which when cooled to 16° to 20° C. contains 1 part of the salt<sup>5</sup>

	after 1 day	in 0.68 parts of water		
„	12 days	„ 2.6	„	„
„	72 „	„ 6.9	„	„
„	7 months	„ 9.7	„	„
„	14 „	„ 8.8	„	„

If the salt is boiled with water, or kept for a considerable time in aqueous solution, it is decomposed into the normal and metatungstates.<sup>7</sup> This accounts for the fact that although the cold fresh solution is neutral in reaction, it gradually becomes acid towards phenolphthalein and alkaline towards tropaeolin, especially after boiling ; it also explains the apparent increase in solubility with time indicated above.

The solution has at first a sweetish taste, but it gradually becomes sharp and bitter. Rosenheim<sup>8</sup> has determined the equivalent conductivities of solutions at 25° C. containing  $\frac{1}{10}$  molecule  $5\text{Na}_2\text{O}.12\text{WO}_3$  in  $v$  litres, as follows :

$v =$	32	64	128	256	512	1024
$\Lambda =$	68.5	79.8	90.8	100.3	110.0	121.8

<sup>1</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>2</sup> Smith, *J. Amer. Chem. Soc.*, 1922, 44, 2027.

<sup>3</sup> von Knorre, *J. prakt. Chem.*, 1883, [2], 27, 49.

<sup>4</sup> Anthon, *loc. cit.*

<sup>5</sup> Marignac, *Comp. rend.*, 1862, 55, 888.

<sup>6</sup> Forcher, *loc. cit.*

<sup>7</sup> von Knorre, *Ber.*, 1885, 18, 2362.

<sup>8</sup> Rosenheim, *loc. cit.* See also Eltzbacher, *Dissertation*, Berlin, 1899.

The following values<sup>1</sup> show the difference in conductivities at 25° C. of freshly prepared cold solutions ( $\Lambda_1$ ), and of solutions previously boiled ( $\Lambda_2$ ).

$v = 25$	50	100
$\Lambda_1 = 61.2$	71.2	78.9
$\Lambda_2 = 82.4$	92.1	99.7

This considerable change, confirmed by Wells,<sup>2</sup> supports Marignac's observation of change in solubility.

(ii)  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 25\text{H}_2\text{O}$ .<sup>3</sup> This hydrate is obtained when crystallisation takes place at about 60° to 80° C.<sup>4</sup> as monoclinic prisms, with axial ratio,

$$a : b : c = 0.8069 : 1 : 0.5328; \text{ and } \beta = 120^\circ 10'.$$

When heated to 100° C. it loses 9.15 per cent. (corresponding to 18 molecules) of water.

(iii)  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 21\text{H}_2\text{O}$  is formed when crystallisation takes place at 100° C. It yields octahedra of the triclinic system,

$$a : b : c = 0.8695 : 1 : 1.2787; \alpha = 91^\circ 18', \beta = 86^\circ 16', \gamma = 97^\circ 59'.$$

The substance is often contaminated with some of the 25-hydrate. At 100° C. it loses 15 molecules  $\text{H}_2\text{O}$ .

(iv)  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$  is obtained, according to Marignac, by crystallisation from a solution of a paratungstate containing sodium carbonate, in short prismatic crystals, triclinic pinacoids,

$$a : b : c = 0.6836 : 1 : 1.1802; \alpha = 95^\circ 3', \beta = 123^\circ 42', \gamma = 91^\circ 53'.$$

Under analogous conditions Forcher<sup>5</sup> obtained octahedral crystals to which he gave the formula  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 15\text{H}_2\text{O}$ . At 100° C. it loses 12 molecules  $\text{H}_2\text{O}$ . It is probably a polymorphous form of the 28-hydrate described above.

(v)  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 21\text{H}_2\text{O}$  crystallises from solutions which have been boiled for some time, yielding prismatic crystals, triclinic pinacoids,

$$a : b : c = 0.9296 : 1 : 0.5207; \alpha = 92^\circ 47', \beta = 96^\circ 28', \gamma = 89^\circ 40'.$$

At 100° C. it loses 17 molecules  $\text{H}_2\text{O}$ .

The acid tungstate,  $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$ , may be prepared<sup>6</sup> by passing carbon dioxide for several days through an aqueous solution of normal sodium tungstate, or by gradually adding formic acid, until the action is distinctly acid, to a solution containing 100 grams of the normal tungstate in 100 c.c. of water. The action of glacial acetic acid on a solution of sodium tungstate produces a mixture of the salts  $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$  and  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$ . The salt,  $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$ , forms monoclinic crystals which effloresce rapidly in

<sup>1</sup> Junius, *Dissertation*, Berlin, 1905.

<sup>2</sup> Wells, *J. Amer. Chem. Soc.*, 1907, 29, 112.

<sup>3</sup> According to Scheibler,  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 14\text{H}_2\text{O}$ .

<sup>4</sup> Marignac, *Ann. Chim. Phys.*, 1864, [4], 3, 5, 76; 1863, [3], 69, 5; *Compt. rend.*, 1864, 58, 809; 1862, 55, 888.

<sup>5</sup> Forcher, *J. prakt. Chem.*, 1862, 86, 227; *Bull. Soc. chim.*, 1863, 5, 197.

<sup>6</sup> Smith, *J. Amer. Chem. Soc.*, 1922, 44, 2027. See also Gibbs, *Proc. Amer. Acad.*, 1880, 15, 1; *Amer. Chem. J.*, 1880, 1, 1, 217. The salt,  $2\text{Na}_2\text{O} \cdot 5\text{WO}_3 \cdot 11\text{H}_2\text{O}$ , probably identical with the above, is described by Marignac, *Compt. rend.*, 1862, 55, 888; *Ann. Chim. Phys.*, 1863, [3], 69, 5; Lefort, *Compt. rend.*, 1876, 82, 1182; *Ann. Chim. Phys.*, 1876, [5], 9, 93; Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

dry air and have density 4.3. When heated, the salt loses 17 molecular proportions of its water of crystallisation at  $100^{\circ}\text{C}$ ., the remainder only being driven off by strong ignition. It melts at  $680.8^{\circ}\text{C}$ . It is soluble in water—19 parts of the salt dissolve in 100 parts of water at ordinary temperature—forming an acid solution.

*Sodium tritungstate*,  $\text{Na}_2\text{O}.3\text{WO}_3.4\text{H}_2\text{O}$ , is prepared, according to Lefort, by gradually adding a concentrated solution of the ditungstate to a boiling 50 per cent. solution of acetic acid. On cooling, a white precipitate results which dissolves in water, and the solution on evaporation yields long prismatic crystals. The existence of a tritungstate is denied by Kantschew.

*Sodium tetratingstate*,  $\text{Na}_2\text{O}.4\text{WO}_3$ , is obtained by the complete dehydration of sodium metatungstate, and is sometimes called "anhydrous sodium metatungstate." As will be seen, however, water is essential to the constitution of metatungstates. The salt may be obtained by heating the paratungstate and treating the residue with water.<sup>1</sup> It is insoluble in water, but on prolonged heating with water at  $120^{\circ}\text{C}$ . it is converted into the metatungstate (see p. 241).

*Sodium pentatungstate*,  $\text{Na}_2\text{O}.5\text{WO}_3$ , is obtained<sup>2</sup> by fusing together sodium tungstate and tungstic anhydride (1 : 2), or by heating sodium paratungstate to incipient fusion and extracting the fused mass with water, when it remains in brilliant plates or scales which are only slightly soluble in water.

*Sodium hexatungstate*,  $\text{Na}_2\text{O}.6\text{WO}_3.9\text{H}_2\text{O}$ , is obtained according to Marignac by prolonged boiling of tungstic acid with sodium paratungstate. Ullik,<sup>3</sup> by decomposing a solution of sodium metatungstate with hydrochloric or nitric acid and allowing the solution to evaporate, obtained large yellowish crystals of what he considered to be the octatungstate,  $\text{Na}_2\text{O}.8\text{WO}_3.12\text{H}_2\text{O}$ , but Friedheim could not confirm his results, and Leontowitsch,<sup>4</sup> using the reagents in different proportions, obtained crystals of the hexatungstate, of composition  $\text{Na}_2\text{O}.6\text{WO}_3.15\text{H}_2\text{O}$ . The anhydrous octatungstate,  $\text{Na}_2\text{O}.8\text{WO}_3$ , was obtained by von Knorre<sup>5</sup> by oxidation of fused metatungstate at a bright red heat, and extraction of the mass with water, when lustrous scales of the octatungstate remain. The relation of these higher acid salts to one another and to metatungstic acid has not yet been determined.

The acid salts,  $2\text{Na}_2\text{O}.3\text{WO}_3.7\text{H}_2\text{O}$ <sup>6</sup> and  $3\text{Na}_2\text{O}.8\text{WO}_3.17\text{H}_2\text{O}$ ,<sup>7</sup> have also been described.

Many double tungstates containing sodium have been obtained<sup>8</sup> (see pp. 213, 222, 224, 225, 232, 233).

**Strontium Tungstates.**—The anhydrous *normal* salt,  $\text{SrWO}_4$ , is precipitated on the addition of strontium acetate solution to a solution

<sup>1</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>2</sup> von Knorre, *ibid.*, 1883, [2], 27, 49.

<sup>3</sup> Ullik, *Sitzungsber. K. Akad. Wiss. Wien*, 1867, 56, ii., 157; *J. prakt. Chem.*, 1868, 103, 147; *Bull. Soc. chim.*, 1869, 11, 50.

<sup>4</sup> Leontowitsch, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 130.

<sup>5</sup> von Knorre, *Ber.*, 1886, 19, 819; *Bull. Soc. chim.*, 1886, 46, 52.

<sup>6</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>7</sup> Wells, *J. Amer. Chem. Soc.*, 1907, 29, 112.

<sup>8</sup> Lotz, *Annalen*, 1851, 91, 49; Marignac, *Compt. rend.*, 1862, 55, 888; *Ann. Chim. Phys.*, 1863, [3], 69, 5; Ullik, *Sitzungsber. K. Akad. Wiss. Wien*, 1867, 56, 148; Gibbs, *Proc. Amer. Acad.*, 1880, 15, 1; *Amer. Chem. J.*, 1880, 1, 217; 1895, 17, 181; von Knorre, *Ber.*, 1886, 19, 821; Hallopeau, *Ann. Chim. Phys.*, 1900, [7], 19, 96.

of a normal alkali tungstate,<sup>1</sup> or it may be obtained in the crystalline form by fusing together strontium chloride, sodium tungstate, and sodium chloride.<sup>2</sup> The crystals are white, translucent, tetragonal bipyramids,  $a : c = 1 : 1.5582$ , and of density 6.184.<sup>3</sup>

*Strontium ditungstate*,  $\text{SrO} \cdot 2\text{WO}_3 \cdot 3\text{H}_2\text{O}$ , is described by Lefort<sup>4</sup> as a white precipitate formed by the addition of strontium acetate to sodium ditungstate solution. It is only slightly soluble in water and becomes anhydrous on heating.

*Strontium paratungstate*,  $3\text{SrO} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$ , is precipitated on adding a hot solution of a paratungstate to a hot solution of strontium chloride or nitrate, using excess of the strontium salt. It is a granular crystalline powder, which does not fuse at red heat.<sup>5</sup> The double salt,  $\text{Na}_2\text{O} \cdot 4\text{SrO} \cdot 12\text{WO}_3 \cdot 29\text{H}_2\text{O}$ , is obtained by adding a strontium salt to a boiling solution of sodium paratungstate<sup>6</sup> until the precipitate no longer redissolves; on filtering and allowing the solution to crystallise, white scales separate. The salt on heating turns yellow but does not fuse.

The salt,  $4\text{SrO} \cdot 10\text{WO}_3 \cdot 26\text{H}_2\text{O}$ , is a white insoluble granular powder<sup>7</sup> obtained in the same way as the corresponding barium and calcium salts. Strontium tritungstate,  $\text{SrO} \cdot 3\text{WO}_3 \cdot 5\text{H}_2\text{O}$ , is described by Lefort.<sup>8</sup>

**Thallium Tungstates.**—The normal thallous salt,  $\text{Tl}_2\text{WO}_4$ , is precipitated when solutions of normal sodium tungstate and a thallous salt are mixed, or when a boiling solution of tungstic acid is neutralised with thallous carbonate.<sup>9</sup> It yields highly refractive, hexagonal micro-crystals. *Thallic tungstate* has not been prepared.

*Thallous paratungstate*,  $5\text{Tl}_2\text{O} \cdot 12\text{WO}_3 \cdot 9\text{H}_2\text{O}$ , is obtained, on adding excess of thallous sulphate solution to a solution of sodium paratungstate,<sup>10</sup> as a white amorphous precipitate, insoluble in water, soluble in alkalis.

**Thorium Tungstate.**—A white flocculent precipitate is formed when a salt of thorium is added to a solution of an alkali tungstate.<sup>11</sup>

**Tin Tungstates.**—*Stannous tungstate*,  $\text{SnWO}_4 \cdot 6\text{H}_2\text{O}$ , is obtained as a yellow powder by mixing solutions of sodium tungstate and stannous chloride.<sup>12</sup> When a solution of ammonio-stannic chloride is added to a solution of ammonium paratungstate, a white flocculent precipitate is formed, presumably of stannic tungstate.<sup>13</sup> It is soluble in excess of the tin salt.

**Tungstic Tungstate**, or the blue oxide of tungsten, is described on p. 200.

**Uranium Tungstate.**—When ammonium tungstate is added to a solution of uranium tetrachloride, a brownish-green precipitate of composition  $\text{U}(\text{WO}_4)_2 \cdot \text{WO}_3 \cdot 6\text{H}_2\text{O}$  is obtained.<sup>14</sup> This compound is used in

<sup>1</sup> Anthon, *J. prakt. Chem.*, 1836, 9, 341; Lefort, *Ann. Chim. Phys.*, 1878, [5], 15, 321.

<sup>2</sup> Schultze, *Annalen*, 1863, 126, 56; Zettnow, *Pogg. Annalen*, 1867, 130, 16, 241.

<sup>3</sup> Zambonini, *Zeitsch. Kryst. Min.*, 1905, 41, 53; Groth, *Chemische Krystallographie*, 1908, ii., 394.

<sup>4</sup> Lefort, *loc. cit.*

<sup>5</sup> von Knorre, *Ber.*, 1885, 18, 326.

<sup>6</sup> Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>7</sup> Smith, *J. Amer. Chem. Soc.*, 1922, 44, 2027.

<sup>8</sup> Lefort, *Ann. Chim. Phys.*, 1879, [5], 17, 470.

<sup>9</sup> Flemming, *Jenaische Zeitsch.*, 1868, 4, 34; *Jahresber.*, 1868, p. 250.

<sup>10</sup> Schaefer, *Dissertation*, Berlin, 1903; *Zeitsch. anorg. Chem.*, 1904, 38, 174.

<sup>11</sup> Berzelius, *Pogg. Annalen*, 1829, 16, 385.

<sup>12</sup> Anthon, *loc. cit.*

<sup>13</sup> Lotz, *Annalen*, 1854, 91, 49.

<sup>14</sup> Rammelsberg, *Pogg. Annalen*, 1843, 59, 31.

the preparation of phosphorescent screens for use in experiments with Röntgen rays.

By the action of uranium sulphate on alkali paratungstates, complex salts of composition  $12\text{Na}_2\text{O} \cdot 6\text{UO}_2 \cdot 8\text{WO}_3 \cdot 25\text{H}_2\text{O}$ ,  $9\text{K}_2\text{O} \cdot 6\text{UO}_2 \cdot 8\text{WO}_3 \cdot 34\text{H}_2\text{O}$ , and a corresponding ammonium salt, have been prepared.<sup>1</sup> Uranyl compounds of composition  $\text{UO}_2 \cdot \text{WO}_4$  and  $\text{UO}_2 \cdot \text{WO}_4 \cdot 2\text{WO}_3 \cdot 5\text{H}_2\text{O}$  are described by Lefort.<sup>2</sup>

**Ytterbium Tungstates.**—Crystalline compounds of composition  $(\text{YbO})_2\text{WO}_4$ ,  $2\text{Yb}_2\text{O}_3 \cdot 4\text{Na}_2\text{O} \cdot 7\text{WO}_3$ , and  $\text{Yb}_2\text{O}_3 \cdot 9\text{Na}_2\text{O} \cdot 12\text{WO}_3$  have been obtained by fusing together ytterbium oxide and tungstic anhydride, with sodium chloride present as a flux.

**Yttrium Tungstate.**—A double tungstate of composition  $\text{Na}_8\text{Y}_2(\text{WO}_4)_7$  has been obtained by dissolving yttrium oxide in fused sodium tungstate.<sup>3</sup>

**Zinc Tungstates.**—The *anhydrous normal* salt,  $\text{ZnWO}_4$ , is obtained as rhombic crystals<sup>4</sup> by fusing together sodium tungstate (1 part), sodium chloride (2 parts), and zinc chloride (2 parts).<sup>5</sup> The *monohydrate*,  $\text{ZnWO}_4 \cdot \text{H}_2\text{O}$ , is obtained by double decomposition as a white amorphous precipitate, slightly soluble in water.<sup>6</sup>

The *ditungstate*,  $\text{ZnO} \cdot 2\text{WO}_3 \cdot 3\text{H}_2\text{O}$ , is obtained as needle-shaped crystals on adding a zinc salt to a solution of sodium ditungstate and concentrating the mixture.<sup>6</sup> It is soluble in 10 parts of water at  $15^\circ \text{C}$ .

*Zinc Paratungstate*,  $5\text{ZnO} \cdot 12\text{WO}_3 \cdot 37\text{H}_2\text{O}$ , may be prepared by the addition of a zinc salt to a solution of sodium paratungstate.<sup>7</sup> It separates as white needle-shaped crystals, which, when heated, turn yellow but do not melt. According to Rosenheim<sup>8</sup> the salt contains 35 molecular proportions of water, of which it loses 28 on heating at  $100^\circ \text{C}$ ., and he therefore formulates the compound as  $\text{Zn}_5(\text{H}_5[\text{H}_2(\text{WO}_4)_6])_2 \cdot 28\text{H}_2\text{O}$ . According to von Knorre,<sup>9</sup> however, the precipitate obtained on adding a solution of zinc sulphate to a boiling solution of sodium paratungstate (in molecular proportions 2 : 1) is a double salt of composition  $\text{Na}_2\text{Zn}_2\text{W}_7\text{O}_{24} \cdot 15\text{H}_2\text{O}$ , while if the temperature of precipitation is below  $60^\circ \text{C}$ ., the salt contains  $21\text{H}_2\text{O}$ . Using ammonium paratungstate,<sup>10</sup> the double salt,  $(\text{NH}_4)_2\text{O} \cdot 2\text{ZnO} \cdot 7\text{WO}_3 \cdot 13\text{H}_2\text{O}$ , has been obtained as white needles.

The *tritungstate*,  $\text{ZnO} \cdot 3\text{WO}_3 \cdot 5\text{H}_2\text{O}$ , and the acid salts,  $9\text{ZnO} \cdot 22\text{WO}_3 \cdot 66\text{H}_2\text{O}$  and  $2\text{ZnO} \cdot 5\text{WO}_3 \cdot 9\text{H}_2\text{O}$ , have been described.<sup>11</sup>

#### METATUNGSTIC ACID AND METATUNGSTATES.

It has already been mentioned (p. 208) that the metatungstates possess characteristic properties which are quite distinct from those of

<sup>1</sup> Gibbs, *Amer. Chem. J.*, 1895, 17, 174.

<sup>2</sup> Lefort, *Compt. rend.*, 1878, 87, 748.

<sup>3</sup> Högbon, *Öfvers. K. Vet.-Akad. Forh.*, 1884, No. 5; *Bull. Soc. chim.*, 1884, [2], 42, 2; *Jahresber.*, 1884, p. 396.

<sup>4</sup> Michel, *Bull. Soc. min. de France*, 1879, 2, 142.

<sup>5</sup> Geuther and Forsberg, *Annalen*, 1861, 120, 270; Zettnow, *Pogg. Annalen*, 1867, 130, 16, 241.

<sup>6</sup> Lefort, *Ann. Chim. Phys.*, 1878, [5], 13, 321.

<sup>7</sup> Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

<sup>8</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139.

<sup>9</sup> von Knorre, *Ber.*, 1886, 19, 819.

<sup>10</sup> Lotz, *Annalen*, 1854, 91, 49.

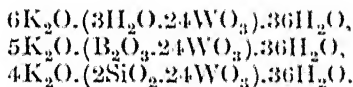
<sup>11</sup> Gibbs, *Amer. Chem. J.*, 1880, 1, 1, 217.



the derivatives of ordinary tungstic acid, and that metatungstic acid is definitely known to exist. The ammonium salt was first obtained by Margueritte,<sup>1</sup> who formulated it as  $(\text{NH}_4)_2\text{O} \cdot 3\text{WO}_3 \cdot 5\text{H}_2\text{O}$ . Laurent<sup>2</sup> first suggested the name "metatungstate," and gave the composition of the ammonium salt as  $5(\text{NH}_4)_2\text{O} \cdot 18\text{WO}_3 \cdot 31\text{H}_2\text{O}$ . That the ratio of base to acid present was  $1\text{R}_2\text{O} : 4\text{WO}_3$  was first recognised by Lotz,<sup>3</sup> and a large number of salts were prepared and examined by Scheibler<sup>4</sup> and Marignac.<sup>5</sup> The former observed that all metatungstates are dehydrated with difficulty, and that the residue after complete expulsion of water at a high temperature no longer possesses the properties of a metatungstate and is insoluble in water.

The dehydration of metatungstates was investigated by Friedheim,<sup>6</sup> who found that the potassium and ammonium salts lost all but 1 molecular proportion of water at  $100^\circ \text{C}$ ., whilst the sodium, barium, manganese, cadmium, and lead salts retained 3 molecular proportions at  $100^\circ \text{C}$ ., and with the exception of the lead salt still contained 1 molecular proportion up to  $220^\circ \text{C}$ . He therefore concluded that part of the water content was water of constitution. However, much difficulty was encountered in determining the actual constitution of the acid and its salts owing to the uncertainty of dehydration experiments at  $100^\circ$  to  $120^\circ \text{C}$ . as a means of determining water content, and because of the difficulty of distinguishing between water of crystallisation and water of constitution.<sup>7</sup>

Further light was brought to the subject, however, by Copaux,<sup>8</sup> who observed that true isomorphism existed between metatungstic acid and the complex heteropolyacids, boron-, phospho-, and silicotungstic acids; and also between certain salts of these acids, for example, the ammonium, potassium, and barium salts. He therefore concluded that these compounds should have similar constitutions, although it was recognised that compounds of high molecular weight occasionally exhibit isomorphism with others which are not of similar constitution. He prepared a new hydrated potassium metatungstate, of composition  $\text{K}_2\text{O} \cdot 4\text{WO}_3 \cdot 6 \cdot 5\text{H}_2\text{O}$  (see p. 240), which was isomorphous with the corresponding borotungstate and silicotungstate, and by increasing the metatungstate formula sixfold, he formulated the three compounds thus:



<sup>1</sup> Margueritte, *J. Pharm. Chim.*, 1845, [3], 7, 222; *Ann. Chim. Phys.*, 1846, [3], 17, 475.

<sup>2</sup> Laurent, *Compt. rend.*, 1847, 25, 538; *Ann. Chim. Phys.*, 1847, [3], 21, 54.

<sup>3</sup> Lotz, *Annalen*, 1854, 91, 49. This was questioned by Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5; and Persoz, *ibid.*, 1864, [4], 1, 93.

<sup>4</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

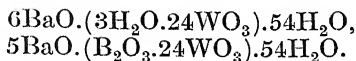
<sup>5</sup> Marignac, *Compt. rend.*, 1862, 55, 888; *Ann. Chim. Phys.*, 1863, [3], 69, 5.

<sup>6</sup> Friedheim, *Dissertation*, Freiburg-im-Breisgau, 1882.

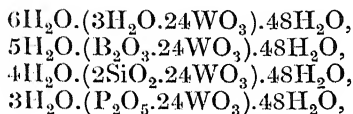
<sup>7</sup> Copaux, *Compt. rend.*, 1908, 147, 973; 1909, 148, 633; *Ann. Chim. Phys.*, 1909, [8], 17, 217; *Zeitsch. anorg. Chem.*, 1911, 70, 297; 1912, 74, 351; Rosenheim and Kohn, *ibid.*, 1911, 69, 247; Rosenheim, *ibid.*, 1911, 70, 418; 1912, 75, 141; Rosenheim and Jänicke, *ibid.*, 1912, 77, 239; Rosenheim and Scherer, *ibid.*, 1914, 89, 224; Rosenheim, *ibid.*, 1915, 93, 273; Rosenheim, Pieck, and Pinsker, *ibid.*, 1916, 96, 139; Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, 26, 1474; Prandtl, *Ber.*, 1915, 48, 692; Prandtl and Hecht, *Zeitsch. anorg. Chem.*, 1915, 92, 198.

<sup>8</sup> Copaux, *Compt. rend.*, 1909, 148, 633.

Similarly he obtained analogous formulæ for the barium salts :

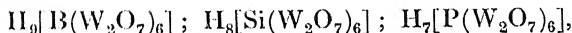


It is to be noticed that the molecular proportion of the base is not the same in the isomorphous compounds, but it is striking that the taking of  $3\text{H}_2\text{O}$  as water of constitution should result in the amounts of water of crystallisation being the same. The idea receives support from the fact that the properties of the metatungstates are remarkably similar to those of the boro-, silico-, and phospho-tungstates ; for example, the salts and their acids are prepared by analogous methods, are readily soluble in water, and are easily crystallised. The free acids were formulated thus :

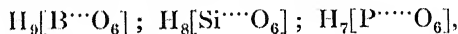


so that metatungstic acid appeared to be a heteropolyacid in which water functioned in the place of an acidic oxide.

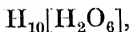
But, as Rosenheim pointed out,<sup>1</sup> the ratio of fixed  $\text{H}_2\text{O}$  to  $\text{WO}_3$  equals 1 : 4 at least, and probably 3 : 4, whereas in the given formula the ratio is only 1 : 8, and this author suggested that a more satisfactory formula might be obtained by regarding the acid as a co-ordinative aquo-compound—in accordance with Werner's views—for example,  $\text{H}_2[\text{WO}(\text{WO}_4)_3 \cdot (\text{H}_2\text{O})_3]$  or  $\text{H}_2[\text{WO}(\text{WO}_4)_3 \cdot \text{H}_2\text{O}]$ . After further investigation<sup>2</sup> Copaux suggested a new formula based on Miolati's views (see p. 164) according to which the heteropolyacids are derived from co-ordinative saturated acids by replacing oxygen atoms by means of complex anions. Thus the boro-, silico- and phospho-tungstic acids are formulated :



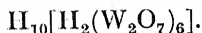
being derived from the hypothetical acids,



the basicity of which is determined by the difference between the valency of the central element and the combined valency of the surrounding six groups. Similarly, the hypothetical acid corresponding to co-ordinative saturated water is



and by substitution the formula for metatungstic acid becomes



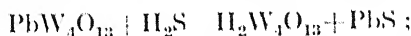
This is in accordance with the general properties and isomorphic relations of the acid and its salts, but such a formula indicates a deca-basic acid, whereas, with the exception of an ill-defined mercury salt (see p. 239), only hexabasic salts,  $\text{M}_6\text{H}_4[\text{H}_2(\text{W}_2\text{O}_7)_6]$ , have been obtained. Even with such a weak base as dimethylpyrone, the salt produced is

<sup>1</sup> Rosenheim and Kohn, *loc. cit.*

<sup>2</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1911, 70, 418; Copaux, *ibid.*, 1911, 70, 297; 1912, 74, 351.

$(C_7H_8O_2)_6 \cdot H_{10}[H_2(W_2O_7)_6]$ . This low basicity may be due to the instability of the anion,<sup>1</sup> but at present needs explanation. However, the above formula appears to conform with our present state of knowledge and is the most satisfactory yet suggested.<sup>2</sup>

**Metatungstic Acid,  $H_2W_4O_{13} \cdot xH_2O$  or  $H_{10}[H_2(W_2O_7)_6] \cdot aq.$** , was first isolated by Scheibler<sup>3</sup> by decomposing the barium salt with dilute sulphuric acid, filtering the mixture, and evaporating the filtrate *in vacuo* over sulphuric acid.<sup>4</sup> It may also be prepared: (1) by decomposing lead metatungstate with hydrogen sulphide:<sup>5</sup>



the excess of hydrogen sulphide is displaced from the filtered solution by passing a stream of carbon dioxide, and then on concentration *in vacuo* small yellow octahedral crystals of metatungstic acid are deposited; (2) by the addition of ether and concentrated hydrochloric (or sulphuric) acid to a concentrated aqueous solution of ammonium metatungstate.<sup>6</sup> The liquid separates into three layers, the lowest of which is yellow and contains the free acid together with ether and the mineral acid. The free metatungstic acid may be obtained by evaporation in a current of air; it separates as crystals of composition  $H_2W_4O_{13} \cdot 8H_2O$  and  $H_2W_4O_{13} \cdot 6H_2O$ .

Metatungstic acid is readily soluble in water and is referred to in the earlier literature as the soluble hydrate of tungstic acid. The aqueous solution, which is colourless, has a marked acid reaction and a pronounced bitter taste. The following table gives the solubility of the acid at different temperatures and the density of the solutions (Soboleff):

Temperature, " C.	Grams $H_2W_4O_{13} \cdot 9H_2O$ <sup>7</sup> in 100 Grams $H_2O$ .	Grams $H_2W_4O_{13}$ <sup>8</sup> in 100 Grams $H_2O$ .	Density.
0	41.5	35.43	1.602
22	88.6	75.65	2.524
43.5	111.9	95.54	3.650

The density of solutions of various concentrations may be deduced from the formula:<sup>9</sup>

$$D_{17.5^\circ C.} = 1 + 0.00903p + 0.0000633p^2 + 0.00000144p^3,$$

where  $p$  = per cent.  $WO_3$  present.

<sup>1</sup> Rosenheim, *Zeitsch. anorg. Chem.*, 1912, **75**, 141.

<sup>2</sup> See also Pfeiffer, *ibid.*, 1919, **105**, 26.

<sup>3</sup> Scheibler, *J. prakt. Chem.*, 1861, **83**, 310; *Bull. Soc. chim.*, 1862, **4**, 256. See also Laurent, *Compt. rend.*, 1847, **25**, 538; *Ann. Chim. Phys.*, 1847, [3], **21**, 54.

<sup>4</sup> See also Péchard, *Ann. Chim. Phys.*, 1891, [6], **22**, 202; Soboleff, *Zeitsch. anorg. Chem.*, 1896, **12**, 16.

<sup>5</sup> Forcher, *Sitzungsber. K. Akad. Wiss. Wien*, 1862, **44**, 164.

<sup>6</sup> Rosenheim and Kohn, *Zeitsch. anorg. Chem.*, 1911, **69**, 247.

<sup>7</sup> This formula, used by Soboleff, is erroneous and does not express the phase in which the solute is present.

<sup>8</sup> Values calculated by present author.

<sup>9</sup> Scheibler, *J. prakt. Chem.*, 1860, **80**, 204; 1861, **83**, 273.

The acid is insoluble in ether except in presence of a mineral acid.<sup>1</sup> With absolute alcohol it yields a colloidal solution.

The crystals of metatungstic acid are isomorphous with the heteropolyacids  $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 26\text{H}_2\text{O}$  and  $\text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot 51\text{H}_2\text{O}$ <sup>2</sup> (see p. 234), and determinations of hydrogen-ion concentration in solutions of the three acids show them to be of about equal strength and somewhat stronger than phosphoric acid.<sup>3</sup> Dilute solutions of metatungstic acid are quite stable in the cold, but more concentrated solutions gradually precipitate the white hydrate,  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ . At 100° C., first white and then yellow tungstic acid separates, even from very dilute solutions.

When a solution of metatungstic acid is electrolysed, it is reduced to a blue solution,<sup>4</sup> lower oxides apparently being formed.

The crystals of metatungstic acid effloresce readily in the air. They have a density of 3.93.<sup>5</sup> On heating, the crystals lose water, becoming anhydrous at about 180° C.

The **metatungstates**,  $\text{M}_2\text{W}_4\text{O}_{13} \cdot \text{aq.}$  or  $\text{M}_6\text{H}_4[\text{H}_2(\text{W}_2\text{O}_7)_6] \cdot \text{aq.}$ , are, with the exception of the lead and mercurous salts, soluble in water. The general methods of preparing the alkali salts are described under potassium metatungstate (p. 240); other metatungstates are usually obtained by the addition of the sulphate of the metal to a solution of barium metatungstate, or by neutralisation of metatungstic acid with the oxide or carbonate. Solutions of metatungstates possess a more bitter taste than those of ordinary tungstates. The salts crystallise only after prolonged evaporation in the cold, whilst from hot solutions gummy residues are obtained on concentration.

In acid solution, metatungstates precipitate alkaloids and other organic bases, while ether in presence of a mineral acid precipitates metatungstic acid.

**Ammonium Metatungstate** yields two hydrates: (1)  $(\text{NH}_4)_2\text{W}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$  or  $(\text{NH}_4)_6\text{H}_4[\text{H}_2(\text{W}_2\text{O}_7)_6] \cdot 21\text{H}_2\text{O}$ , and (2)  $(\text{NH}_4)_2\text{W}_4\text{O}_{13} \cdot 6\text{H}_2\text{O}$ .

The former is obtained (1) by prolonged heating of crystalline ammonium paratungstate at 250° C., when ammonia is expelled, the residue then being dissolved in water and allowed to crystallise;<sup>6</sup> (2) by boiling a solution of ammonium paratungstate for several days and then allowing to crystallise;<sup>7</sup> (3) by the addition of nitric acid to a solution of an acid tungstate of ammonium, filtering and allowing to evaporate (Laurent); this product is contaminated with ammonium nitrate which can be removed only with difficulty.

Ammonium metatungstate crystallises in large, lustrous, tetragonal octahedra, with axial ratio  $a : c = 1 : 1.012$ ,<sup>8</sup> isomorphous with the potassium salt and with ammonium borotungstate,  $5(\text{NH}_4)_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot 52\text{H}_2\text{O}$ . The crystals, which are colourless and transparent,

<sup>1</sup> Rosenheim and Kohn, *loc. cit.* Compare Soboleff, *Zeitsch. anorg. Chem.*, 1896, 12, 16.

<sup>2</sup> Copaux, *Ann. Chim. Phys.*, 1909, [8], 17, 207.

<sup>3</sup> Rosenheim and Brauer, *Zeitsch. anorg. Chem.*, 1915, 93, 273.

<sup>4</sup> Leiser, *Zeitsch. Elektrochem.*, 1907, 13, 690.

<sup>5</sup> Soboleff, *loc. cit.*

<sup>6</sup> Scheibler, *loc. cit.*; Persoz, *Ann. Chim. Phys.*, 1864, [4], 1, 93; Marignac, *ibid.*, 1864, [4], 3, 71.

<sup>7</sup> Laurent, *Ann. Chim. Phys.*, 1847, [3], 21, 54; Lotz, *Annalen*, 1854, 91, 49; Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5; Taylor, *J. Amer. Chem. Soc.*, 1902, 24, 629. See also Margueritte, *Ann. Chim. Phys.*, 1846, [3], 17, 475.

<sup>8</sup> Copaux, *Ann. Chim. Phys.*, 1909, [8], 17, 207.

on heating melt in the water of crystallisation and at  $100^{\circ}\text{C}$ . lose 7 molecular proportions of water; the remaining molecule is not expelled below  $200^{\circ}\text{C}$ . The salt begins to lose ammonia at  $120^{\circ}\text{C}$ ., and at  $250^{\circ}\text{C}$ . it is converted into a glass-like "colloidal" tungstate (see p. 213) of composition  $(\text{NH}_4)_2\text{W}_6\text{O}_{19}\cdot 4$  or  $6\text{H}_2\text{O}$ .<sup>1</sup>

It dissolves in water: 1 part of salt in 0.84 part of water at  $15^{\circ}\text{C}$ .,<sup>2</sup> and 1 part of salt in 0.35 part of water at  $45^{\circ}\text{C}$ .<sup>3</sup> The solution is nearly neutral and is highly refractive. The salt is insoluble in alcohol or ether.

The *hexahydrate*,  $(\text{NH}_4)_2\text{W}_4\text{O}_{13}\cdot 6\text{H}_2\text{O}$ , is formed by treating a hot solution of the salt with alcohol and allowing the mixture to cool, when it separates in monoclinic prisms. Its crystallographic elements are

$$a : b : c = 0.8121 : 1 : 0.7963 ; \beta = 95^{\circ} 9'.$$

At  $100^{\circ}\text{C}$ . it loses 5 molecular proportions of water.<sup>4</sup>

An *acid salt*,  $3(\text{NH}_4)_2\text{O}\cdot 16\text{WO}_3\cdot 17\text{H}_2\text{O}$ , separates as colourless crystals on evaporating a solution of the metatungstate containing hydrochloric acid.<sup>4</sup> The crystals rapidly effloresce in the air, and at  $100^{\circ}\text{C}$ . lose about  $13\text{H}_2\text{O}$ . The salt yields an acid solution with water, which on evaporation deposits the metatungstate again.

A *double compound* of composition  $(\text{NH}_4)_2\text{W}_4\text{O}_{13}\cdot \text{NH}_4\text{NO}_3\cdot 2\text{H}_2\text{O}$  separates on evaporating a solution containing ammonium metatungstate and excess of ammonium nitrate.<sup>5</sup> It yields hexagonal prisms which are decomposed by water.

**Barium Metatungstate**,  $\text{BaW}_4\text{O}_{13}\cdot 9\text{H}_2\text{O}$  or  $\text{Ba}_3\text{H}_4[\text{H}_2(\text{W}_2\text{O}_7)_6]\cdot 25\text{H}_2\text{O}$ ,<sup>6</sup> is prepared by mixing boiling concentrated solutions of sodium metatungstate and barium chloride in the presence of a little hydrochloric acid and allowing to cool. The resulting crystals contain some tritungstate, but this can be removed by recrystallisation. The crystals are lustrous, milky-white, rhombic bipyramids, with axial ratio  $a : b : c = 0.9962 : 1 : 1.5070$ ,<sup>7</sup> and isomorphous with barium borotungstate (see p. 234). Density 4.298 at  $14^{\circ}\text{C}$ . The salt is decomposed by water. When heated to  $100^{\circ}\text{C}$ . it loses two-thirds of the water present.

**Beryllium Metatungstate** has been obtained in fine laminae which are very deliquescent.

**Cadmium Metatungstate**,  $\text{CdW}_4\text{O}_{13}\cdot 10\text{H}_2\text{O}$ , is formed by the addition of barium metatungstate to a solution of cadmium sulphate.<sup>8</sup> It yields lustrous octahedral crystals with axial ratio  $a : c = 1 : 0.9936$ .<sup>9</sup> It is stable in the air, and on heating at  $100^{\circ}$  to  $110^{\circ}\text{C}$ . it loses  $7\text{H}_2\text{O}$ , the remaining water only being expelled at a much higher temperature.<sup>10</sup>

**Calcium Metatungstate**,  $\text{CaW}_4\text{O}_{13}\cdot 10\text{H}_2\text{O}$ , is formed by the

<sup>1</sup> Taylor, *J. Amer. Chem. Soc.*, 1902, 24, 629.      <sup>2</sup> Lotz, *Annalen*, 1854, 91, 49.

<sup>3</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5.

<sup>4</sup> Marignac, *Ann. Chim. Phys.*, 1864, [4], 3, 71.

<sup>5</sup> Marignac, *Compt. rend.*, 1862, 55, 888; *Ann. Chim. Phys.*, 1863, [3], 69, 5; Friedheim, *Dissertation*, Freiburg-im-Breisgau, 1882.

<sup>6</sup> Different estimates of the amount of water present have been given by Zettnow, *Pogg. Annalen*, 1867, 130, 16, 241; Wyruboff, *Bull. Soc. franç. Min.*, 1892, 15, 63; Copaux, *Ann. Chim. Phys.*, 1909, [8], 17, 207; *Zeitsch. anorg. Chem.*, 1912, 74, 351.

<sup>7</sup> Wyruboff, *loc. cit.*; Groth, *Chemische Kristallographie*, 1908, ii., 609.

<sup>8</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>9</sup> Wyruboff, *loc. cit.*

<sup>10</sup> Friedheim, *loc. cit.*

action of a hot solution of metatungstic acid on calcium carbonate.<sup>1</sup> It crystallises with difficulty, yielding triclinic pinacoidal crystals,

$$a : b : c = 1.0070 : 1 : 1.3694 ; \alpha = 91^\circ 1' ; \beta = 93^\circ 0' ; \gamma = 90^\circ 16'.$$

**Cerium Metatungstate**,  $\text{Ce}_2(\text{W}_4\text{O}_{13})_3 \cdot 30\text{H}_2\text{O}$ , yields triclinic pinacoidal prisms<sup>3</sup> which are stable in air at ordinary temperatures.

**Cobalt Metatungstate**,  $\text{CoW}_4\text{O}_{13} \cdot 9\text{H}_2\text{O}$ , is obtained by double decomposition.<sup>1</sup> According to Wyruboff, the crystals contain  $9 \cdot 5\text{H}_2\text{O}$  and are rhombic bipyramids, with axial ratio,

$$a : b : c = 0.9878 : 1 : 1.3764.$$

**Copper Metatungstate**,  $\text{CuW}_4\text{O}_{13} \cdot 11\text{H}_2\text{O}$ , is obtained by Scheibler's method, and yields laminae and tables which probably belong to the monoclinic system. It forms a compound with ammonia (see p. 213).

**Ferrous Metatungstate**, prepared by dissolving iron in metatungstic acid, is crystallisable<sup>1</sup> but difficult to obtain pure. The ferric salt cannot be obtained by crystallisation.

**Lead Metatungstate**,  $\text{PbW}_4\text{O}_{13} \cdot 5\text{H}_2\text{O}$ , is obtained as a white flocculent precipitate by double decomposition.<sup>4</sup> It is insoluble in water; soluble in hot nitric acid. However, by the addition of lead nitrate to an alkali tungstate solution, a crystalline precipitate has been obtained,<sup>5</sup> of composition  $\text{PbW}_4\text{O}_{13} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ . This is only very slightly soluble in water, and when heated it loses  $7\text{H}_2\text{O}$ .

**Lithium Metatungstate** cannot be prepared by either of Scheibler's methods, *i.e.* by neutralising metatungstic acid with lithium carbonate, or by adding lithium sulphate to a solution of barium metatungstate. The anhydrous tetratungstate has been prepared (see p. 220).

**Magnesium Metatungstate**,  $\text{MgW}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$ , is obtained by double decomposition.<sup>1</sup> It yields lustrous monoclinic prisms with<sup>2</sup>

$$a : b : c = 0.6763 : 1 : 0.7792 ; \beta = 106^\circ 43'.$$

**Manganous Metatungstate**,  $\text{MnW}_4\text{O}_{13} \cdot 10\text{H}_2\text{O}$ , is also obtained by double decomposition. It forms beautiful light yellow quadratic octahedra,  $a : c = 1 : 0.9919$ ,<sup>2</sup> permanent in the air. On heating at  $100^\circ \text{C}$ . to  $110^\circ \text{C}$ . it loses  $7\text{H}_2\text{O}$ , the remaining  $3\text{H}_2\text{O}$  only being expelled at a much higher temperature.<sup>6</sup>

**Mercurous Metatungstate**,  $\text{Hg}_2\text{W}_4\text{O}_{13} \cdot 25\text{H}_2\text{O}$  (?), is obtained, according to Scheibler, on adding mercurous nitrate to the free acid or to an alkali metatungstate, as a white bulky precipitate which shrinks considerably on drying and assumes a lemon-yellow colour. Friedheim, however, was only able to obtain the paratungstate by this means, while Copaux<sup>7</sup> by treating concentrated metatungstic acid with mercurous nitrate solution obtained crystals in which the ratio  $\text{Hg}_2\text{O} : \text{WO}_3$  was equal to  $1.7 : 4$ . A compound of composition

<sup>1</sup> Scheibler, *loc. cit.*

<sup>2</sup> Wyruboff, *loc. cit.*

<sup>3</sup> Scheibler, *loc. cit.* ; Wyruboff, *loc. cit.*

<sup>4</sup> Scheibler, *loc. cit.* ; Friedheim, *loc. cit.*

<sup>5</sup> Rosenheim and Kohn, *Zeitsch. anorg. Chem.*, 1911, 69, 247.

<sup>6</sup> Friedheim, *loc. cit.*

<sup>7</sup> Copaux, *Zeitsch. anorg. Chem.*, 1912, 74, 351.

$9\text{Hf}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot \text{N}_2\text{O}_5 \cdot 29\text{H}_2\text{O}$  was also obtained. This may be formulated as  $\text{Hf}_2\text{O}_3 \cdot \text{H}_2[\text{H}_2(\text{W}_2\text{O}_7)_6] \cdot \text{Hf}_2\text{NO}_3 \cdot 12 \cdot 5\text{H}_2\text{O}$ , which is of interest in that the metatungstic acid exhibits a higher basicity than is usual.

**Nickel Metatungstate**,  $\text{NiW}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$ , is formed by double decomposition <sup>1</sup> and yields monoclinic prisms and tables with crystallographic data,<sup>2</sup>

$$a : b : c = 0.6555 : 1 : 0.7464 ; \beta \quad 106^\circ 22'.$$

**Potassium Metatungstate** may be prepared by the following methods :

(1) A solution of the paratungstate is boiled with excess of the yellow tungstic acid until the filtered solution no longer gives a precipitate with hydrochloric acid.<sup>3</sup> It is then concentrated and allowed to crystallise slowly over sulphuric acid.

(2) A large excess of acetic acid is added to a saturated solution of potassium paratungstate. A heavy oily layer, consisting of a concentrated solution of the metatungstate, forms at the bottom of the vessel.<sup>4</sup>

(3) A mineral acid in concentrated solution is added to the paratungstate solution until the precipitate no longer redissolves.<sup>4</sup> The solution is then concentrated and allowed to crystallise.

(4) An aqueous solution of normal potassium tungstate is electrolysed in a cell in which the electrodes are separated by a diaphragm.<sup>5</sup> When the anodic solution contains sufficient tungstic acid the metatungstate is formed.

Potassium metatungstate usually crystallises as the *octahydrate*,  $\text{K}_2\text{W}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$ , i.e.  $\text{K}_6\text{H}_4[\text{H}_2(\text{W}_2\text{O}_7)_6] \cdot 24\text{H}_2\text{O}$ , yielding tetragonal octahedra,<sup>2</sup> which effloresce and at  $100^\circ \text{C}$ . lose seven-eighths of the water present.

Long needle-shaped crystals are also occasionally obtained<sup>6</sup> which are probably identical with the hydrate,  $\text{K}_2\text{W}_4\text{O}_{13} \cdot 6 \cdot 5\text{H}_2\text{O}$ , obtained by Copaux<sup>7</sup> in hexagonal prisms, with axial ratio  $a : b \quad 1 : 0.659$ , isomorphous with potassium boro- and silico-tungstates (see p. 234). These crystals, like their isomorphs, exhibit dextrorotatory power,  $[\alpha]_D = +9^\circ$ .

The *pentahydrate*,  $\text{K}_2\text{W}_4\text{O}_{13} \cdot 5\text{H}_2\text{O}$ , is obtained<sup>8</sup> by adding alcohol to a solution of the metatungstate, and warming the mixture until the precipitate redissolves ; on cooling the resulting solution, monoclinic prisms separate. These crystals are not efflorescent and are readily soluble in water. Their crystallographic data are

$$a : b : c = 0.5945 : 1 : 0.6609 ; \beta \quad 123^\circ 0'.$$

When heated at  $100^\circ \text{C}$ . they lose 4 molecular proportions of water.

**Rubidium Metatungstate**,  $\text{Rb}_2\text{W}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$ , is formed by double decomposition and yields efflorescent tetragonal crystals, with axial ratio  $a : c = 1 : 0.9702$ .<sup>2</sup>

<sup>1</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204 ; 1861, 83, 273.

<sup>2</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1892, 15, 63.

<sup>3</sup> Scheibler, *loc. cit.* ; Copaux, *Ann. Chim. Phys.*, 1909, [8], 17, 207.

<sup>4</sup> Marguerite, *Ann. Chim. Phys.*, 1846, [3], 17, 475.

<sup>5</sup> Schaefer, *Zeitsch. anorg. Chem.*, 1904, 38, 142 ; Lottermoser, *Kolloid. Zeitsch.*, 1922, 30, 346.

<sup>6</sup> Scheibler, *loc. cit.* ; Marignac, *Compt. rend.*, 1862, 55, 888 ; *Ann. Chim. Phys.*, 1863, [3], 69, 5.

<sup>7</sup> Copaux, *Compt. rend.*, 1909, 148, 633.

<sup>8</sup> Marignac, *loc. cit.*

**Samarium Metatungstate**,  $\text{Sa}_2(\text{W}_4\text{O}_{13})_3 \cdot 35\text{H}_2\text{O}$ , is formed by double decomposition. The crystals are readily soluble in water.

**Silver Metatungstate**,  $\text{Ag}_2\text{W}_4\text{O}_{13} \cdot 3\text{H}_2\text{O}$ , is prepared by mixing together boiling solutions containing equivalent quantities of sodium metatungstate and silver nitrate in the presence of a little nitric acid. On cooling, the solution deposits a crust consisting of microscopic octahedra, which readily dissolve in water and may be recrystallised (by allowing the solution to evaporate) over sulphuric acid. The salt decomposes on heating.

**Sodium Metatungstate**,  $\text{Na}_3\text{W}_4\text{O}_{13} \cdot 10\text{H}_2\text{O}$ , is obtained by methods analogous to those described for the potassium salt. The salt crystallises in colourless glistening tetragonal bipyramids, with axial ratio  $a : c = 1 : 0.9930$ ,<sup>1</sup> isomorphous with ammonium, cadmium, and manganese metatungstates,<sup>2</sup> and of density 4.04.<sup>3</sup> The crystals are very efflorescent, and if placed over sulphuric acid lose most of their water. When heated they lose  $7\text{H}_2\text{O}$  per molecule at  $120^\circ \text{C}$ .<sup>4</sup> and at  $240^\circ \text{C}$ . only  $1\text{H}_2\text{O}$  remains, the residue after heating at this temperature being still soluble in water. The remaining water is removed at red heat, and the residue is insoluble.

One part of water at ordinary temperature dissolves 10.69 parts of salt, and the resulting solution has density 3.019,<sup>5</sup> whilst at  $19^\circ \text{C}$ . one part of the salt dissolves in 0.195 part of water.<sup>6</sup> The solubility increases greatly with temperature. The equivalent conductivities of solutions containing one gram-equivalent in  $v$  litres at  $25^\circ \text{C}$ . have been determined<sup>7</sup> as follows:

$v = 32$	64	128	256	512	1024
$\Lambda = 89.3$	98.7	107.6	116.6	126	134.1

According to Schön<sup>8</sup> cotton which has been soaked in a solution of sodium metatungstate immediately becomes blue in daylight, but the colour disappears in the dark.

A colloidal form of sodium metatungstate is obtained<sup>9</sup> when a solution of normal sodium tungstate is treated with hydrochloric acid in the proportion of  $2\text{Na}_2\text{WO}_4 : 3\text{HCl}$ , and the mixture subjected to dialysis. According to Graham colloidal tungstic acid is obtained by this method (see p. 206), but all the soda cannot be removed by dialysis; and according to Sabanéeff the solution remaining in the dialyser always contains  $1\text{Na}_2\text{O} : 4\text{WO}_3$ . On evaporation of this solution an amorphous product is obtained which appears identical in properties with the crystalline metatungstate. Biltz and Vegesack,<sup>10</sup> after prolonged dialysis, obtained a solution containing  $2\text{Na}_2\text{O} : 11\text{WO}_3$  and expressed the opinion that colloidal tungstic acid was present.

**Strontium Metatungstate**,  $\text{SrW}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$ , is prepared<sup>5</sup> by

<sup>1</sup> Rammelsberg, *Handbuch krist.-physik. Chem.*, i., 579 (1881).

<sup>2</sup> Wyruboff, *loc. cit.*

<sup>3</sup> Soboleff, *Zeitsch. anorg. Chem.*, 1896, 12, 16. According to Scheibler, 3.847 at  $13^\circ \text{C}$ .

<sup>4</sup> Friedheim, *Dissertation*, Freiburg-im-Breisgau, 1882. See also Sabanéeff, *Zeitsch. anorg. Chem.*, 1897, 14, 354. <sup>5</sup> Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273.

<sup>6</sup> Forcher, *J. prakt. Chem.*, 1862, 86, 227; *Bull. Soc. chim.*, 1863, [1], 5, 197.

<sup>7</sup> Soboleff, *loc. cit.* For vapour-pressure determinations see Tammann, *Mém. Acad. St Pétersbourg*, 1887, [7], 35.

<sup>8</sup> Schön, *Jahresber.*, 1893, p. 136.

<sup>9</sup> Sabanéeff, *Zeitsch. anorg. Chem.*, 1897, 14, 354.

<sup>10</sup> Biltz and Vegesack, *Zeitsch. physikal. Chem.*, 1910, 68, 376.



saturating a hot solution of metatungstic acid with strontium carbonate. It crystallises in monoclinic prisms, with crystallographic data,<sup>1</sup>

$$a : b : c = 1.0556 : 1 : 0.7999; \beta = 40^\circ 21'.$$

**Thallous Metatungstate**,  $\text{Ti}_2\text{W}_4\text{O}_{13} \cdot 3\text{H}_2\text{O}$ , is obtained<sup>2</sup> in a similar manner to the analogous silver salt. It is a yellowish-white, almost insoluble, crystalline powder which loses 2 molecular proportions of water at  $90^\circ \text{C}$ .

**Zinc Metatungstate**,  $\text{ZnW}_4\text{O}_{13} \cdot 10\text{H}_2\text{O}$ , is obtained by the addition of zinc sulphate to a solution of the barium salt.<sup>3</sup> It forms readily soluble crystals, according to Wyrouboff monoclinic prisms, with

$$a : b : c = 1.6626 : 1 : 0.7557; \beta = 105^\circ 57'.$$

If the salt is crystallised between  $6^\circ \text{C}$ . and  $20^\circ \text{C}$ . it contains<sup>4</sup> only  $8\text{H}_2\text{O}$ .

#### PERTUNGSTIC ACID AND PERTUNGSTATES.

By the action of hydrogen peroxide on solutions of tungstic acid and tungstates, compounds analogous to the persulphuric acids and persulphates are obtained. By dissolving tungsten trioxide in a 2 per cent. hydrogen peroxide solution at the boiling-point, and evaporating the resulting solution, a yellow amorphous mass results,<sup>5</sup> of composition  $\text{WO}_3 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  and soluble in water to an acid solution.

Several sodium salts have been prepared:

$\text{Na}_2\text{W}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$  is obtained<sup>6</sup> as white radiating crystals by the addition of hydrogen peroxide to a hot solution of sodium paratungstate and evaporation of the mixture in a vacuum. The crystals are easily soluble in water.

$\text{Na}_2\text{W}_2\text{O}_9 \cdot 6\text{H}_2\text{O}$  results as a yellowish-white crystalline powder when the above mixture of paratungstate and hydrogen peroxide is precipitated with alcohol.<sup>7</sup> In this salt the ratio of  $\text{WO}_3$  to active oxygen, as determined by titration with potassium permanganate in sulphuric acid solution, is 1 : 1, whilst in the above dihydrate it is 2 : 1; this suggests that the latter is derived from an acid of constitution  $2\text{WO}_3 \cdot \text{H}_2\text{O}_2$ , *i.e.*  $\text{H}_2\text{W}_2\text{O}_8$ , and the former from an acid of constitution  $\text{WO}_3 \cdot \text{H}_2\text{O}_2$ , *i.e.*  $\text{H}_2\text{WO}_6$ , of which  $\text{H}_2\text{W}_2\text{O}_9$  is an anhydro-acid (*i.e.*  $2\text{H}_2\text{WO}_5 - \text{H}_2\text{O}$ ).<sup>8</sup>

By the addition of cooled hydrogen peroxide and aqueous sodium hydroxide solutions to a cooled solution of sodium pertungstate, prepared according to the former method described above, precipitating with alcohol at  $-12^\circ \text{C}$ . and drying the resulting product in the air, compounds of composition  $\text{Na}_2\text{O}_2 \cdot \text{WO}_4 \cdot \text{H}_2\text{O}_2$  and  $\text{Na}_2\text{O}_2 \cdot \text{WO}_4 \cdot \text{H}_2\text{O}_2 + (\text{Na}_2\text{O}_2)_2\text{WO}_4 + 7\text{H}_2\text{O}$  have been obtained.<sup>9</sup> These are unstable

<sup>1</sup> Wyrouboff, *Bull. Soc. franç. Min.*, 1892, **15**, 63; Groth, *Chemische Krystallographie*, 1908, ii., 609.

<sup>2</sup> Rosenheim and Kohn, *Zeitsch. anorg. Chem.*, 1911, **69**, 247.

<sup>3</sup> Scheibler, *J. prakt. Chem.*, 1860, **80**, 204; 1861, **83**, 273.

<sup>4</sup> Wyrouboff, *loc. cit.*

<sup>5</sup> Cammerer, *Chem. Zeit.*, 1891, **15**, 957; Fairley, *Trans. Chem. Soc.*, 1877, **31**, 141;

Pissarjewsky, *Zeitsch. anorg. Chem.*, 1900, **24**, 108.

<sup>6</sup> Péchard, *Compt. rend.*, 1891, **112**, 1060. See also Piñera-Alvarez, *Chem. News*, 1906, **94**, 269.

<sup>7</sup> Pissarjewsky, *loc. cit.*

<sup>8</sup> See Price, *Per-acids and their Salts* (Longmans, 1912).

<sup>9</sup> Melikoff and Pissarjewski, *Ber.*, 1898, **31**, 632.

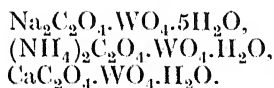
compounds, although more stable than the corresponding molybdenum compounds (see p. 157); they gradually lose oxygen on standing in air, whilst water causes rapid evolution of oxygen, hydrogen peroxide being found in the resulting solution.

The potassium salt,  $\text{K}_2\text{O}_4\cdot\text{WO}_4\cdot\text{H}_2\text{O}$ , is similarly produced by the action of hydrogen peroxide and potash on potassium pertungstate. It is more stable than the sodium salts, but explodes when rubbed or heated to  $80^\circ\text{C}$ .

The following compounds containing peroxidic oxygen have also been described:

**Potassium Fluoroxypertungstate**,  $2\text{KF}\cdot\text{WO}_3\text{F}_2\cdot\text{H}_2\text{O}$ .<sup>1</sup>

**Sodium, Ammonium, and Calcium "Ozotungsten" Oxalates:**<sup>2</sup>



**Sodium "Ozotungsten" Tartrate.**<sup>3</sup>

#### TUNGSTEN BRONZES.

The compounds known as tungsten bronzes are reduction products of the tungstates of the alkali and alkaline earth metals. Their exact constitution is not known, but it is generally recognised that the molecule contains several hexavalent tungsten atoms and one tetravalent tungsten atom, and may be represented by the formula  $\text{R}'_2\text{O}\cdot(\text{WO}_3)_x$ .  $\text{WO}_2$ . The empirical formula accordingly becomes  $\text{R}'_2(\text{WO}_3)_{x+1}$ .

The substances have been designated as tungsten bronzes because, owing to their remarkable properties, they may be used as substitutes for bronze powders. They all possess extremely vivid colours and are quite insoluble in water. Strong acids, including hydrofluoric acid, do not attack them; even hot aqua regia has only slight action. They are decomposed, however, by fusion with alkali, sulphur,<sup>4</sup> ammonium persulphate, or ammonium hydrogen sulphate.

The bronzes may be obtained by the following methods:

(1) Reduction of an acid tungstate by heating in hydrogen<sup>4</sup> or coal gas, or by fusion with metallic tin,<sup>5</sup> zinc, or iron.

(2) Electrolytic reduction of a fused acid tungstate;<sup>6</sup> or of a fused mixture of tungstic acid with the requisite quantity of a metallic carbonate;<sup>7</sup> or of a solution of tungstic acid in a fused mixture of alkali chlorides,<sup>8</sup> the ratio of tungstic acid to chloride being greater than 1 : 2 (see p. 184).

(3) Synthesis by fusing together a metallic tungstate, either acid or normal, with tungsten dioxide, in absence of air.<sup>9</sup>

The bronzes are obtained in the crystalline form, generally as cubes

<sup>1</sup> Piccini, *Zeitsch. anorg. Chem.*, 1892, **2**, 21.

<sup>2</sup> Mazzucchelli and Inghillieri, *Atti R. Accad. Lincei*, 1908, [5], **17**, ii., 30.

<sup>3</sup> Mazzucchelli and Borghi, *Gazzetta*, 1910, **40**, ii., 241.

<sup>4</sup> Wöhler, *Pogg. Annalen*, 1824, **2**, 345.

<sup>5</sup> Wright, *Annalen*, 1851, **79**, 221.

<sup>6</sup> Scheibler, *loc. cit.*; Stavenhagen, *Ber.*, 1899, **32**, 3064.

<sup>7</sup> Engels, *Zeitsch. anorg. Chem.*, 1903, **37**, 125.

<sup>8</sup> L. and H. H. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 51.

<sup>9</sup> Brunner, *Dissertation*, Zürich, 1903.

or needles, and exhibit colours ranging from golden yellow to violet and dark blue, a metallic lustre also being sometimes evident. The colour sometimes varies according to whether the bronze is dry or moist, and suspensions of a finely powdered bronze often show by transmitted light the colour which is complementary to its usual colour. The bronzes show metallic properties in being of high density, 6.5 to 7.5, and excellent conductors of electricity. The difficulties which are encountered in the analysis of the tungstates (see p. 208) are enhanced in the case of the bronzes by their insolubility and resistance to ordinary reagents. The difficulty of determining whether a product is homogeneous or not, and the fact that the same method of preparation will sometimes give totally different products when repeated, lead to doubt as to whether many of the bronzes described in the literature are definite compounds. For example, von Knorre, by fusing together equal molecular proportions of sodium and potassium paratungstates, and heating the mass to redness in hydrogen, obtained on one occasion a purple-red sodium-potassium bronze to which he ascribed the composition  $2\text{Na}_4\text{W}_5\text{O}_{15} \cdot 5\text{K}_2\text{W}_4\text{O}_{12}$ , and on another occasion a darker red bronze of composition  $2\text{Na}_2\text{W}_3\text{O}_9 \cdot 3\text{K}_2\text{W}_4\text{O}_{12}$ .<sup>1</sup>

The bronzes are generally analysed by first oxidising completely to tungstate and then determining the amount of metal and tungstic acid in the product. It is therefore necessary that the oxidation should be really complete and not merely superficial as when the bronze is heated in the air—a method which has sometimes been employed. Wöhler suggested heating the bronze with sulphur, decomposing the mass with aqua regia, and estimating the alkali metal and tungstic acid in separate portions of the liquid. A more satisfactory method is due to Philipp.<sup>2</sup> The finely powdered bronze is boiled with a large excess of ammoniacal silver nitrate solution, and silver is precipitated which is ignited and weighed. The silver always contains a little tungstic acid, which is left as a residue on treating with nitric acid and can be weighed. The tungsten and sodium are estimated in the filtrate from the silver. In this reaction the quantity of silver precipitated is always proportional to the amount of oxygen necessary for the complete oxidation of the bronze, so that the ratio  $\text{WO}_2 : \text{WO}_3$  is accurately obtained. If the bronze is rich in tungsten it is necessary to heat the mixture to about  $120^\circ \text{C}$ . in order to obtain complete decomposition. This reduction of silver nitrate by bronzes is remarkable in view of their stability towards ordinary oxidising agents.

The following bronzes have been described :<sup>3</sup>

**Lithium Tungsten Bronze,  $\text{Li}_2\text{W}_5\text{O}_{15}$ ,** obtained by fusion of lithium paratungstate with tin<sup>4</sup> or by electrolysis of fused lithium paratungstate ;<sup>5</sup> deep blue microscopic prisms.

Bronzes of composition  $\text{Li}_2\text{W}_4\text{O}_{12}$  and  $\text{Li}_2\text{W}_7\text{O}_{21}$  are described by Brunner.<sup>6</sup>

**Lithium Potassium Tungsten Bronze,  $\text{Li}_2\text{W}_5\text{O}_{15} \cdot 3\text{K}_2\text{W}_4\text{O}_{12}$ ,** is

<sup>1</sup> von Knorre, *J. prakt. Chem.*, 1883, [2], 27, 49.

<sup>2</sup> Philipp, *Ber.*, 1882, 15, 499.

<sup>3</sup> Smithells (*Trans. Chem. Soc.*, 1922, 121, 2236) suggests the possible formation of a thorium tungsten bronze in the tungsten filament lamp.

<sup>4</sup> von Knorre, *J. prakt. Chem.*, 1883, [2], 27, 49; Hallopeau, *Compt. rend.*, 1898, 127, 512.

<sup>5</sup> Stavenhagen, *Ber.*, 1899, 32, 3064.

<sup>6</sup> Brunner, *Dissertation*, Zürich, 1903.

obtained as violet needles by reducing with tin a fused mixture containing lithium and potassium tungstates in molecular proportions.<sup>1</sup>

**Potassium Tungsten Bronze**,  $K_2W_4O_{12}$ , is obtained<sup>2</sup> by fusing together potassium carbonate and tungstic acid and reducing the mass by coal gas, hydrogen, or tin; or by electrolysis of the fused paratungstate.<sup>3</sup> It yields reddish-violet prisms of density 7.1; a suspension appears blue by transmitted light and green by reflected light. According to von Knorre and Schaefer<sup>4</sup> this is the only potassium bronze which exists; other bronzes, for example  $K_2W_3O_9$  and  $K_2W_5O_{15}$ , have, however, been described.<sup>5</sup>

Two **potassium sodium tungsten bronzes** have been prepared<sup>6</sup> (see above),  $5K_2W_4O_{12} \cdot 2Na_4W_5O_{15}$  and  $3K_2W_4O_{12} \cdot 2Na_2W_3O_9$ . Both are dark red; the former has density 7.117 and when powdered becomes blue.

**Sodium tungsten bronzes** have been the subject of much investigation<sup>7</sup> and many have been described. The following appear to be well-defined compounds:  $Na_2W_2O_6$ , golden-yellow cubic crystals, density 7.28;  $Na_2W_3O_9$ , reddish-purple octahedra, density 7.22;  $Na_2W_4O_{12}$ , violet needles, density 7.195;  $Na_2W_5O_{15}$ , blue cubic crystals;  $Na_4W_5O_{15}$ , reddish-yellow crystals; and  $Na_5W_6O_{18}$ , yellow cubes.

Engels<sup>8</sup> has described a series of bronzes containing an alkali and an alkaline earth metal. These were prepared by electrolysis of the mass obtained by fusing commercial sodium or potassium tungstate with the calculated amount of metal carbonate.

$2BaW_4O_{12} \cdot 3Na_2W_5O_{15}$ , dark blue crystals.

$BaW_4O_{12} \cdot 5Na_2W_3O_9$ , yellow-red cubes.

$BaW_4O_{12} \cdot 5K_2W_4O_{12}$ , dark red pyramids.

$SrW_4O_{12} \cdot 5Na_2W_5O_{15}$ , brilliant violet pyramids.

$SrW_4O_{12} \cdot 12Na_2W_3O_9$ , carmin-red pyramids.

$SrW_4O_{12} \cdot 5K_2W_4O_{12}$ , red pyramids.

$CaW_4O_{12} \cdot 5Na_2W_5O_{15}$ , violet pyramids.

$CaW_4O_{12} \cdot 10Na_2W_3O_9$ , purple cubes or pyramids.

$CaW_4O_{12} \cdot 5K_2W_4O_{12}$ , glistening red pyramids.

#### TUNGSTEN AND SULPHUR.

Tungsten forms two sulphides of composition  $WS_2$  and  $WS_3$ .

**Tungsten Disulphide**,  $WS_2$ , occurs native in the mineral *tungstenite* (see p. 182). It may be prepared by heating tungsten hexachloride in a current of hydrogen sulphide at 375° to 550° C.;<sup>9</sup> by fusing together pure dry potassium carbonate, flowers of sulphur, and tungsten trioxide;<sup>10</sup> or by strongly heating tungsten trioxide with

<sup>1</sup> Feit, *Ber.*, 1888, 21, 133.

<sup>2</sup> Schaefer, *Zeitsch. anorg. Chem.*, 1904, 38, 142.

<sup>3</sup> von Knorre, *loc. cit.*

<sup>4</sup> von Knorre and Schaefer, *Ber.*, 1902, 35, 3407.

<sup>5</sup> Hallopeau, *Compt. rend.*, 1898, 127, 57; *Bull. Soc. chim.*, 1899, [3], 21, 267; Brunner, *loc. cit.*

<sup>6</sup> von Knorre, *loc. cit.*; Feit, *loc. cit.*  
<sup>7</sup> See Wöhler, *Pogg. Annalen*, 1824, 2, 345; Malaguti, *Ann. Chim. Phys.*, 1835, [2], 60, 271; Wright, *Annalen*, 1851, 79, 221; Scheibler, *J. prakt. Chem.*, 1860, 80, 204; 1861, 83, 273; Philipp and Schwebel, *Ber.*, 1879, 12, 2234; Philipp, *loc. cit.*; Brunner, *loc. cit.*; L. and H. H. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, 1924, 46, 51.

<sup>8</sup> Engels, *Zeitsch. anorg. Chem.*, 1903, 37, 125.

<sup>9</sup> Defacqz, *Ann. Chim. Phys.*, 1901, [7], 22, 239.

<sup>10</sup> Riche, *ibid.*, 1857, [3], 50, 5; Defacqz, *loc. cit.*

excess of mercuric sulphide,<sup>1</sup> or with sodium thiosulphate,<sup>2</sup> or (with or without the addition of carbon) in a current of hydrogen sulphide, or of sulphur or carbon disulphide vapour.<sup>3</sup> It is also formed by direct synthesis, by strongly heating metallic tungsten and sulphur.<sup>4</sup>

Tungsten disulphide is a soft, lustrous, dark grey crystalline powder, of density 7.5 at 10° C. When heated in air it yields the trioxide, but if heated out of contact with air it loses sulphur only at high temperatures, the temperature of the electric furnace being necessary to reduce it to the metal. When heated in hydrogen it is completely reduced at 800° to 900° C. It is attacked by fluorine at ordinary temperatures, yielding the fluoride. Chlorine at 400° C. yields tungsten hexachloride. Bromine attacks the sulphide at 700° C. Hydrogen chloride has no action.

The disulphide is insoluble in water and in most acids. Aqua regia has little action; but a mixture of nitric acid and hydrofluoric acid dissolves it readily. It is readily decomposed by molten alkalis.<sup>5</sup>

**Tungsten Trisulphide,  $WS_3$ ,** may be obtained by treating a solution of an alkali thiotungstate (see below) with excess of acid.<sup>6</sup> The thiotungstate may first be obtained by fusing wolframite (3 parts) with sodium sulphate (7 parts) and carbon (1.2 parts).<sup>7</sup> The mass is extracted with water and the solution treated with excess of sulphuric or hydrochloric acid. The precipitate is filtered rapidly, washed with water containing hydrogen sulphide, and dried at 100° C. in a current of carbon dioxide.<sup>8</sup> It is necessary to exclude air as much as possible or the product is found to contain oxygen.

Tungsten trisulphide is a brown powder which becomes black when dried. When heated in absence of air it gives up sulphur and forms the disulphide  $WS_2$ . It may be reduced to the metal by heating with lime in an electric furnace.<sup>9</sup> When heated in the air it yields tungsten trioxide. It is slightly soluble in cold water, more readily in hot, forming a colloidal solution (see below). It is easily soluble in alkali hydroxides, carbonates, and sulphides,<sup>8</sup> forming dark brown solutions which contain thiotungstates and colloidal tungsten trisulphide.

*Colloidal Tungsten Trisulphide.* It was observed by Berzelius<sup>10</sup> that when the freshly precipitated trisulphide is washed with water, it dissolves to a slight extent, forming a yellow solution. If the precipitate is boiled with pure water it dissolves in considerable quantity, yielding a brownish-yellow solution. Winssinger<sup>11</sup> obtained a dark brown solution of tungsten trisulphide by adding to a solution of sodium thiosulphate a little more dilute hydrochloric acid than was

<sup>1</sup> Wöhler and Uslar, *Annalen*, 1855, 94, 255.

<sup>2</sup> Faktor, *Pharm. Post*, 1905, 38, 527.

<sup>3</sup> Riche, *Ann. Chim. Phys.*, 1857, [3], 50, 5.

<sup>4</sup> von Borch, *Öfvers. K. Vet.-Akad. Forh.*, 1851, p. 149; *Jahresber.*, 1851, p. 344; *J. prakt. Chem.*, 1851, 54, 254.

<sup>5</sup> Defacqz, *Compt. rend.*, 1899, 128, 609.

<sup>6</sup> Berzelius, *Schweigger's J.*, 1816, 16, 476; *Ann. Chim. Phys.*, 1821, [2], 17; *Pogg. Annalen*, 1825, 4, 147; 1826, 8, 267; Uslar, *Annalen*, 1855, 94, 225; Corleis, *ibid.*, 1886, 232, 244; *Bull. Soc. chim.*, 1887, 47, 190.

<sup>7</sup> Uslar, *loc. cit.*; Weiss, Martin, and Stimmelmayer, *Zeitsch. anorg. Chem.*, 1910, 65, 279.

<sup>8</sup> Corleis, *loc. cit.*

<sup>9</sup> Weiss, Martin, and Stimmelmayer, *loc. cit.*

<sup>10</sup> Berzelius, *Lehrbuch der Chemie*, 3rd ed., 1833, iii., 126.

<sup>11</sup> Winssinger, *Bull. Soc. chim.*, 1888, [2], 49, 452; *Bull. Acad. roy. Belg.*, 1888, 15, 390.

necessary to saturate the alkali. The solution could be passed through filter paper. On boiling, or on the addition of electrolytes, the trisulphide is precipitated.

The existence of oxysulphides of tungsten, described by Berzelius and others,<sup>1</sup> is doubtful.

A **sulphochloride** of tungsten,  $3\text{WS}_3\cdot\text{WCl}_6$ , has been obtained<sup>2</sup> by heating the hexachloride with liquid hydrogen sulphide in a sealed tube for thirty-six hours at  $60^\circ$  to  $65^\circ$  C. It is a brown powder, insoluble in carbon disulphide, alcohol, or benzene; it is decomposed by water. If heated to redness in the air, it takes fire. It is readily oxidised by nitric acid or fused potash.

**Thiotungstates.**<sup>3</sup>—By substituting sulphur for oxygen in tungstates the following types of compounds have been obtained:  $\text{R}_2\text{WO}_3\text{S}$ ,  $\text{R}_2\text{WO}_2\text{S}_2$ ,  $\text{R}_2\text{WOS}_3$ ,  $\text{R}_2\text{WS}_4$ . These are produced:

(1) By dissolving the hydrate of tungstic acid in an alkali hydrosulphide.

(2) By the action of hydrogen sulphide on solutions or suspensions of alkali or neutral tungstates.

(3) By fusing a tungstate with sulphur.

The compounds are generally yellow to yellowish brown in colour and yield well-defined crystals which are soluble in water. The solution, on addition of an acid, deposits tungsten trisulphide.

*Potassium monothiotungstate*,  $\text{K}_2\text{WO}_3\text{S}\cdot\text{H}_2\text{O}$ , is the only salt of this type which has been isolated. It is produced<sup>4</sup> by passing hydrogen sulphide into a concentrated solution of potassium tungstate until a slight yellow precipitate is formed. A large bulk of alcohol is then added, and colourless deliquescent crystals are deposited. The salt is soluble in water, and the solution gives a white precipitate with zinc sulphate.

*Ammonium dithiotungstate*,  $(\text{NH}_4)_2\text{WO}_2\text{S}_2$ , is obtained as yellow crystals when hydrogen sulphide is passed into a strong ammoniacal solution of ammonium tungstate. The crystals are triclinic pinacoids,<sup>5</sup> with axial ratio  $a : b : c = 0.703 : 1 : 0.3392$ . The salt is stable when dry, but decomposes when moist.

*Potassium dithiotungstate*,  $\text{K}_2\text{WO}_2\text{S}_2$ , is formed by fusing together potassium tungstate and sulphur in absence of air<sup>6</sup> and extracting with water. It yields lemon-yellow rectangular crystals, which lose water on heating, and if out of contact with air, melt without decomposition.

*Potassium trithiotungstate*,  $\text{K}_2\text{WOS}_3\cdot\text{H}_2\text{O}$ , is obtained in quadratic plates by the prolonged action of hydrogen sulphide on potassium tungstate. It is very soluble in water, but may be precipitated by means of alcohol. The crystals deliquesce in a damp atmosphere and effloresce in a dry one. The solution gives a lemon-yellow precipitate with zinc sulphate.

*Normal ammonium thiotungstate*,  $(\text{NH}_4)_2\text{WS}_4$ , is prepared by the prolonged action of hydrogen sulphide on a dilute solution of ammonium

<sup>1</sup> Corl is, *loc. cit.*; Winssinger, *loc. cit.*

<sup>2</sup> Defacqz, *loc. cit.*

<sup>3</sup> Berzelius, *Pogg. Annalen*, 1826, 8, 267; Corl is, *loc. cit.*

<sup>4</sup> Corl is, *loc. cit.*

<sup>5</sup> Kalkowsky, *Zeitsch. Kryst. Min.*, 1888, 13, 32; Groth, *Chemische Kristallographie*, 1908, ii., 663.

<sup>6</sup> Berzelius, *loc. cit.*

tungstate. It forms transparent, orange-coloured crystals, rhombic bipyramidal, with axial ratio  $a : b : c = 0.778 : 1 : 0.5675$ , isomorphous with ammonium thiomolybdate.<sup>1</sup> The salt is stable when dry. When heated in an atmosphere of carbon dioxide, tungsten disulphide remains; it is slowly reduced to the metal when heated in hydrogen.

*Normal potassium thiotungstate*,  $K_2WS_4$ , is prepared in a similar manner to the ammonium salt; or it may be precipitated by adding potassium hydrogen sulphide and alcohol to a solution of the ammonium salt. The crystals are rhombic bipyramids,<sup>2</sup> with axial ratio<sup>3</sup>  $a : b : c = 0.7495 : 1 : 0.5665$ . It is readily soluble in water. On heating, it melts without decomposition.

The compound,  $K_2WS_4 \cdot KNO_3$ , is described by Berzelius.

*Normal sodium thiotungstate*,  $Na_2WS_4$ , is prepared by similar reactions to the above. The crystals are very hygroscopic, and are exceedingly soluble in water. The solutions of normal thiotungstates are not precipitated by zinc sulphate. Sodium thiotungstate is soluble in alcohol.

*Thiotungstates of calcium, strontium, and barium* have been prepared<sup>4</sup> by the action of hydrogen sulphide on suspensions of the corresponding tungstates, whereby yellow solutions were obtained from which the thiotungstates could be crystallised.

The free acids corresponding to the above salts have not been isolated.

#### TUNGSTEN AND SELENIUM.

Two selenides, of composition  $WSe_2$  and  $WSe_3$ , have been obtained.<sup>5</sup>

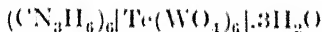
**Tungsten Diselenide**,  $WSe_2$ , is formed as a grey substance when the triselenide is heated.

**Tungsten Triselenide**,  $WSe_3$ , is produced by the addition of acids to the reddish-brown solution obtained by passing in hydrogen selenide to a solution of sodium acid tungstate. The precipitate, after drying, is glossy black. On heating, it yields selenium and tungsten diselenide. It dissolves readily in alkalis.

#### TUNGSTEN AND TELLURIUM.

Tellurides of tungsten are not known.

The guanidinium salt of a heteropolyacid tellurotungstic acid of composition



has been described.<sup>6</sup> The metallic salts have not been studied,<sup>7</sup> nor has the acid been isolated.

#### TUNGSTEN AND NITROGEN.

**Nitrides and Related Products.** Metallic tungsten may be heated in nitrogen gas to a temperature of  $1500^\circ C$ . without any forma-

<sup>1</sup> Corl  is, *Annalen*, 1886, 232, 244; Vater, *Zeitsch. Kryst. Min.*, 1885, 10, 392.

<sup>2</sup> Kalkowsky, *Zeitsch. Kryst. Min.*, 1888, 13, 32.

<sup>3</sup> Corl  is, *loc. cit.*

<sup>4</sup> Berzelius, *Lehrbuch der Chemie*, 3rd ed., 1883, iii., 126.

<sup>5</sup> Uelsmann, *Jahresber.*, 1860, p. 92.

<sup>6</sup> Haeblerle, *Dissertation*, Berlin, 1911, p. 14.

<sup>7</sup> See Klein, *Bull. Soc. chim.*, 1884, 42, 169.

tion of nitride.<sup>1</sup> In ammonia gas, tungsten is slightly affected at 850° C., a mere trace of nitride being formed.<sup>2</sup> However, if the oxide of tungsten is heated under pressure in a mixture of hydrogen and nitrogen, tungsten nitride is produced.<sup>3</sup> According to Langmuir,<sup>4</sup> nitrogen does not, at any temperature, react with solid tungsten, but when a tungsten lamp containing nitrogen at low pressures is run for some time, the nitrogen gradually disappears. This takes place in three ways :

(1) Nitrogen combines with tungsten vapour to form the nitride  $WN_2$ .

(2) As the electric discharge passes through the nitrogen, the nitride  $WN_2$  is formed at the hot tungsten cathode.

(3) At very low pressures and high voltages nitrogen is driven on to the glass in such a form that it can be recovered by heating.

The *dinitride*,  $WN_2$ , is a clear brown powder, stable *in vacuo* at 400° C., but is decomposed at 2150° C. It is decomposed by water, yielding ammonia and probably the oxide  $WO_3$ .

Other nitrides have been described, but the literature concerning them is somewhat contradictory. By the action of ammonia on tungstic anhydride and tungsten hexachloride various products have been obtained. Wöhler<sup>5</sup> found that when the anhydride was heated in a stream of dry ammonia a black compound was obtained, which he named tungsten nitretamidoxide, considering it to be a mixed compound of nitride, amide, and oxide, of composition  $4WN_2.W_2(NH_2)_2.2WO_2 = W_8N_{10}H_4O_2$ . Rideal,<sup>6</sup> however, by similar means, obtained a black amorphous product of composition  $W_5N_6H_3O_5$ . At a higher temperature this compound yields metallic tungsten. Liquid ammonia does not react with tungstic anhydride even when the mixture is heated to 108° C. under pressure.<sup>7</sup>

If tungstic anhydride is heated in a crucible with ammonium chloride, repeated additions of the latter compound being made until a product of constant weight is obtained, a black substance results<sup>8</sup> which appears to be an oxynitride of composition  $WO_3.WN_2$ .

The *sesquinitride*,  $W_2N_3$ , is, according to Rideal,<sup>9</sup> obtained as a black powder by the action of dry ammonia on tungsten hexachloride. The reaction takes place in the cold, and the product is freed from ammonium chloride by washing with water. The nitride has a semi-metallic lustre, is insoluble in nitric acid, but is oxidised by aqua regia to tungstic acid. When heated in the air it glows and is converted into yellow tungstic anhydride. Wöhler<sup>10</sup> regarded the product obtained by the action of ammonia on tungsten hexachloride as a mixture of two compounds to which he gave the formulæ  $W_3N_4H_4 = 2WN.W(NH_2)_2$  and  $W_3N_6H_4 = 2WN_2.W(NH_2)_2$ . The latter can be converted to the former by heating in hydrogen, and both at 1000° C. yield metallic tungsten. If the compound  $W_3N_6H_4$  is heated just above its temperature of formation in ammonia, a nitride of composition  $W_3N_2$  is obtained.<sup>11</sup>

<sup>1</sup> Sieverts and Bergner, *Ber.*, 1911, 44, 2394.

<sup>2</sup> Henderson and Galletly, *J. Soc. Chem. Ind.*, 1908, 27, 387.

<sup>3</sup> German Patent, 259647 (1913).

<sup>4</sup> Langmuir, *J. Amer. Chem. Soc.*, 1913, 35, 931.

<sup>5</sup> Wöhler, *Annalen*, 1850, 73, 190.

<sup>6</sup> Rideal, *Trans. Chem. Soc.*, 1889, 55, 41.

<sup>7</sup> Rosenheim and Jacobsohn, *Zeitsch. anorg. Chem.*, 1906, 50, 297.

<sup>8</sup> Rideal, *loc. cit.* Cf. Desi, *J. Amer. Chem. Soc.*, 1897, 19, 213.

<sup>9</sup> Rideal, *loc. cit.*

<sup>10</sup> Wöhler, *loc. cit.* See also *Annalen*, 1858, 105, 258.

<sup>11</sup> Uhrlaub, *Die Verbindungen einiger Metalle mit Stickstoff*, Göttingen, 1859.



By heating tungstyl chloride,  $\text{WO}_2\text{Cl}_2$ , with dry ammonia, a black compound of composition  $\text{W}_4\text{O}_4\text{N}_4\text{H}_2$  is obtained.<sup>1</sup> This is insoluble in water, dilute alkalis, or hydrochloric acid. It is decomposed by concentrated nitric acid, and yields ammonia with potassium hydroxide. It reduces silver nitrate solution to metallic silver. By the action of liquid ammonia on tungstyl chloride, a brown compound,  $\text{WO}_3 \cdot 3\text{NH}_3$  (see p. 213), is obtained.<sup>2</sup>

### TUNGSTEN AND PHOSPHORUS.

**Tungsten Phosphides.**—The combination of tungsten and phosphorus was first studied by Pelletier<sup>3</sup> who, however, did not publish any exact data. The later investigations of Wright and Defacqz appear to have established the existence of four definite phosphides.

**Tungsten Diphosphide,  $\text{WP}_2$ .**—This compound is prepared<sup>4</sup> by heating tungsten hexachloride at  $450^\circ$  to  $500^\circ$  C. in a current of dry hydrogen phosphide. The product is washed with carbon disulphide to remove any free phosphorus present. The phosphide is obtained in black crystals, of density 5.8, insoluble in water, and in the usual organic solvents. It is stable in air, but decomposes on fusion. When heated in hydrogen to  $600^\circ$  C. partial reduction occurs, but at  $900^\circ$  C. phosphorus still remains, probably as the phosphide  $\text{WP}$ . The halogens react vigorously on heating; it burns brilliantly in oxygen at  $450^\circ$  C. Many metals reduce it to tungsten at high temperatures, e.g. copper, zinc, or iron at  $1000^\circ$  C. Hydrofluoric and hydrochloric acids do not attack it, but a mixture of either of these acids with nitric acid dissolves it readily. When fused with alkali carbonate, a mixture of phosphate and tungstate is obtained.

**Tritungsten Tetraphosphide,  $\text{W}_3\text{P}_4$ .**—By passing phosphorus vapour over metallic tungsten heated to redness a grey powder of composition  $\text{W}_3\text{P}_4$  is obtained.<sup>5</sup> It is stable in air and is oxidised with difficulty.

**Tungsten Monophosphide,  $\text{WP}$ .**—This phosphide is prepared by heating the diphosphide  $\text{WP}_2$  (1 part) with copper phosphide (20 to 30 parts) at  $1200^\circ$  C. for three or four hours with careful exclusion of air; <sup>6</sup> the resulting mass is treated with dilute nitric acid, and the phosphide remains in the form of grey lustrous prisms of density 8.5. The compound is stable in air and behaves in a similar manner to the diphosphide towards oxygen, the halogens, acids, and alkalis, but it may be heated in hydrogen to  $900^\circ$  C. without reduction taking place.

**Tungsten Subphosphide,  $\text{W}_4\text{P}_2$ .**—By strongly heating a mixture of phosphoric acid and tungstic anhydride in a carbon crucible, lustrous steel-coloured crystals of this phosphide are obtained.<sup>7</sup> The crystals are six-sided prisms of density 5.21. It conducts electricity well, is very stable in air even at higher temperatures, and is very resistant to acids. When heated in a current of oxygen it burns brilliantly. It dissolves in a fused mixture of alkali carbonate and nitrate.

<sup>1</sup> Smith and Shinn, *Zeitsch. anorg. Chem.*, 1893, 4, 381.

<sup>2</sup> Rosenheim and Jacobsohn, *ibid.*, 1906, 50, 297.

<sup>3</sup> Pelletier, *Ann. Chim. Phys.*, 1792, [1], 13, 137.

<sup>4</sup> Defacqz, *Compt. rend.*, 1900, 130, 915; *Ann. Chim. Phys.*, 1901, [7], 22, 238.

<sup>5</sup> Wright, *Annalen*, 1851, 79, 244.

<sup>6</sup> Defacqz, *Compt. rend.*, 1901, 132, 32; *Ann. Chim. Phys.*, 1901, [7], 22, 238.

<sup>7</sup> Wöhler, *J. Chem. Soc.*, 1853, 5, 94; Wright, *loc. cit.*

**Heteropolyacids of Tungsten and Phosphorus: the Phosphotungstic Acids.**—Tungstic acid behaves similarly to molybdic acid in combining with phosphoric acid to form series of complex phosphotungstates of varying composition analogous to the phosphomolybdates (see p. 163). It was first noticed by Scheibler<sup>1</sup> that a solution of sodium tungstate containing phosphoric acid was able to precipitate certain organic compounds, and he isolated two acids in which he considered the proportion  $P_2O_5 : WO_3$  to be 1 : 6 and 1 : 20 respectively. Salts of these acids were also prepared,<sup>2</sup> and Gibbs<sup>3</sup> suggested the formula  $8H_2O.P_2O_5.20WO_3.aq.$  for the second acid. This author also postulated the existence of six different series of compounds in which for 1 molecule of  $P_2O_5$  there were respectively 24, 22, 20, 18, 16, and 14 molecules of  $WO_3$ . The acid corresponding to the first of these series was soon isolated and described,<sup>4</sup> but the existence of all of them has not been proved, whilst other series containing less tungstic acid have also been shown to exist.<sup>5</sup>

**12-Tungstophosphoric Acid,  $H_7[P(W_2O_7)_6].xH_2O$ ,** ordinary phosphotungstic acid, ( $P_2O_5 : WO_3 = 1 : 24$ ), is analogous to 12-molybdophosphoric acid (see p. 164) and similar to metatungstic acid (see p. 236). It may be prepared<sup>6</sup> by dissolving 500 grams of pure sodium tungstate and 250 grams of sodium phosphate crystals in 500 c.c. of water and evaporating until a skin forms on the surface; 750 c.c. of hydrochloric acid are then added and the mixture again evaporated and allowed to cool, when the acid may be shaken out with ether.<sup>7</sup> After evaporating the ether and crystallising from water, the acid is obtained<sup>8</sup> in large octahedral crystals of composition  $H_7[P(W_2O_7)_6].28H_2O$ . This hydrate is not stable at ordinary temperatures and readily changes into a 22-hydrate, which crystallises in rhombohedra from solutions maintained at 50° C. The 28-hydrate may be kept in a stable condition at ordinary temperatures by the addition of 1 per cent. of the stable 28-hydrate of 12-molybdophosphoric acid. If concentrated nitric acid is added to a solution of the acid, small prismatic crystals of a 19-hydrate are precipitated.<sup>9</sup> The acid melts at about 90° C. It is very soluble in water, yielding dense solutions. The equivalent conductivities of solutions containing  $\frac{1}{2}$  molecule in  $v$  litres at 25° C. have been found<sup>10</sup> to be :

$v = 32$	64	128	256	512	1024
$\Lambda = 168.9$	181.0	198.4	220.3	249.3	274.5

<sup>1</sup> Scheibler, *Ber.*, 1872, 5, 801; *Bull. Soc. chim.*, 1873, 19, 23.

<sup>2</sup> Zettnow, *Pogg. Annalen*, 1867, 130, 259.

<sup>3</sup> Gibbs, *Ber.*, 1877, 10, 1384; *Bull. Soc. chim.*, 1878, 30, 31; *Amer. Chem. J.*, 1895, 17, 167; *Bull. Soc. chim.*, 1895, [3], 14, 1176.

<sup>4</sup> Sprenger, *J. prakt. Chem.*, 1880, [2], 22, 418.

<sup>5</sup> Kehrman, *Ber.*, 1887, 20, 1805, 1811; *Bull. Soc. chim.*, 1887, 48, 502; 1889, [3], 2, 19; *Annalen*, 1888, 245, 45, 57; Kehrman and Mellet, *Helv. Chim. Acta*, 1922, 5, 942; Péchard, *Compt. rend.*, 1889, 108, 1167; 109, 301; 1890, 110, 754; *Bull. Soc. chim.*, 1890, [3], 3, 802; Soboleff, *Zeitsch. anorg. Chem.*, 1896, 12, 16.

<sup>6</sup> See also Gibbs, *loc. cit.*; Sprenger, *loc. cit.*; *Bull. Soc. chim.*, 1881, [2], 36, 221; Brandhorst and Kraut, *Annalen*, 1888, 249, 373; *Bull. Soc. chim.*, 1890, [3], 3, 87; Péchard, *Compt. rend.*, 1889, 109, 301.

<sup>7</sup> Drechsel, *Ber.*, 1887, 20, 1452.

<sup>8</sup> This method of separation is much used in the isolation of complex compounds, and is usually associated with the name of Drechsel.

<sup>9</sup> Soboleff, *loc. cit.*; Copaux, *Ann. Chim. Phys.*, 1909, [8], 17, 251; Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1912, 77, 239; 1917, 101, 254.

<sup>10</sup> Rosenheim and Jänicke, *loc. cit.*

The hydrogen-ion concentration in a 0.005 N solution<sup>1</sup> is  $4.1 \times 10^{-3}$ . The formula for the acid given above suggests that its basicity should be 7, and the neutralisation curves of solutions with sodium hydroxide show that it is at least hexabasic. However, only acid salts of the metals have been prepared, but the normal guanidinium salt,  $(\text{CN}_3\text{H}_6)_7[\text{P}(\text{W}_2\text{O}_7)_6] \cdot 12\text{H}_2\text{O}$ , has been obtained by the addition of guanidinium carbonate to the free acid.<sup>2</sup>

The alkali salts of this acid may be prepared :

- (1) By the addition of the alkali hydroxide or carbonate to a solution of the free acid ;
- (2) By saturation of a boiling solution of alkali phosphate with tungstic anhydride ; or
- (3) By the addition of a mineral acid, preferably hydrochloric acid, to a solution of alkali tungstate containing a small quantity of alkali phosphate.

The salts obtained correspond to the general formula  $3\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot x\text{H}_2\text{O}$  ( $\text{R} = \text{NH}_4, \text{K}, \text{Na}$ ). The ammonium and potassium salts are white, crystalline, almost insoluble powders ; the sodium salt yields large transparent crystals<sup>3</sup> which become opaque on exposure to air and are readily soluble in water. The latter salt forms two hydrates,<sup>4</sup> the one stable at ordinary temperatures having the composition  $\text{Na}_3\text{H}_4[\text{P}(\text{W}_2\text{O}_7)_6] \cdot 13\text{H}_2\text{O}$ , whilst at lower temperatures a hydrate containing  $19\text{H}_2\text{O}$  is the stable form. That these salts are acid salts and not normal is confirmed by equivalent conductivity measurements. The corresponding salts of barium, copper, and silver have been prepared,<sup>5</sup> as also have the more strongly acid salts,  $2\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot 59\text{H}_2\text{O}$ ,  $\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot 59\text{H}_2\text{O}$ , and  $\text{Ag}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot 60\text{H}_2\text{O}$  ; the silver salts are insoluble in water. In some of the earlier literature salts of this series are described under formulæ of the type  $x\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 20\text{WO}_3 \cdot y\text{H}_2\text{O}$ . Phosphotungstic acid and the phosphotungstates are used as reagents for the precipitation of alkaloids and proteins,<sup>6</sup> and react with many other organic compounds.<sup>7</sup> The acid is also used as a clarifying agent in urine analysis.<sup>8</sup> Potassium and ammonium salts may be detected by means of phosphotungstic acid, with which they give insoluble precipitates.

**11-Tungstophosphates** ( $\text{P}_2\text{O}_5 : \text{WO}_3 = 1 : 22$ ).—The free acid corresponding to this series of salts has not been isolated. The salts are very stable and are obtained by careful hydrolysis of the 12-tungsto-

<sup>1</sup> Brauer, *Dissertation*, Berlin, 1918.

<sup>2</sup> Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1912, 77, 239 ; 1917, 101, 254.

<sup>3</sup> Kehrman and Freinkel, *Ber.*, 1891, 24, 2326.

<sup>4</sup> Sprenger, *J. prakt. Chem.*, 1880, [2], 22, 432 ; Kehrman and Freinkel, *loc. cit.* ; Gibbs, *Amer. Chem. J.*, 1880, 2, 217 ; Rosenheim and Jänicke, *loc. cit.* ; Soboleff, *Zeitsch. anorg. Chem.*, 1896, 12, 16.

<sup>5</sup> Sprenger, *loc. cit.*  
<sup>6</sup> Winterstein, *Chem. Zeit.*, 1898, 22, 539 ; Wechsler, *Zeitsch. physiol. Chem.*, 1911, 73, 138 ; Jacobs, *J. Biol. Chem.*, 1912, 12, 429 ; Guglielmelli, *Anal. Soc. Quim. Argentina*, 1918, 6, 57.

<sup>7</sup> Folin and Denis, *J. Biol. Chem.*, 1912, 12, 239, 245 ; Funk and Macallum, *Biochem. J.*, 1913, 7, 356. See also Levine, *Science*, 1920, 52, 391 ; Funk, *Biochem. Bull.*, 1916, 5, 1 ; Drummond, *Biochem. J.*, 1918, 12, 5 ; Heiduschka and Wolff, *Schweiz. Apoth.-Zeit.*, 1920, 58, 213, 229 ; *Chem. Zentr.*, 1921, ii, 840, 841.

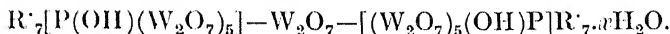
<sup>8</sup> May, *J. Biol. Chem.*, 1912, 11, 81 ; Oppler, *Zeitsch. physiol. Chem.*, 1911, 75, 71 ; Folin and Macallum, *J. Biol. Chem.*, 1912, 11, 265 ; 1912, 13, 363 ; Funk and Macallum, *loc. cit.*

phosphates.<sup>1</sup> If barium carbonate is added to a 30 per cent. solution of 12-tungstophosphoric acid until a faint turbidity appears, on concentration a white barium salt separates which may be recrystallised from solution in dilute acetic acid. The crystals obtained are of composition  $7\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 22\text{WO}_3 \cdot 54\text{H}_2\text{O}$ .

The *potassium salt*,  $7\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 22\text{WO}_3 \cdot 3\text{H}_2\text{O}$ , may be obtained in a similar manner by adding potassium carbonate to a suspension of the potassium 12-tungstophosphate until a clear solution is obtained.

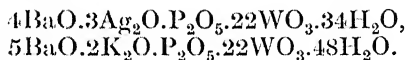
The *sodium salt*,  $7\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 22\text{WO}_3 \cdot 33\text{H}_2\text{O}$ , is best prepared by adding sodium sulphate to a solution of the barium salt. On evaporating the filtered solution a mass of needle-shaped crystals is obtained.

These salts are all soluble in water, and the solutions react neutral to litmus. Acid salts of this series have not been obtained. The addition of strong mineral acids to 11-tungstophosphates causes decomposition into the 12-tungstophosphate and the 21 : 2-tungstophosphate (see below); the following formula has therefore been suggested<sup>2</sup> as an expression of their constitution:



The molecule is thus considered to contain two nuclei joined by an outer bridge.

The following well-crystallised double salts have been prepared<sup>3</sup> by addition of simple metallic salts to solutions of 11-tungstophosphates:



A series of salts obtained by the addition of hydrochloric acid to mixtures of alkali tungstates and alkali phosphates have been described by Gibbs,<sup>4</sup> who formulates them,  $3\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 22\text{WO}_3 \cdot x\text{H}_2\text{O}$ . From their mode of preparation and reactions these salts appear to be more related to the 12-tungstophosphates than to the salts just described. Their composition, however, is not established.

**21 : 2-Tungstophosphoric Acid**, ( $\text{P}_2\text{O}_5 : \text{WO}_3 = 1 : 21$ ),<sup>5</sup> may be obtained by heating the ammonium salt with aqua regia; nitrogen is evolved and a solution is obtained from which the acid separates on cooling. It may also be prepared from barium 11-tungstophosphate by precipitation of the barium with sulphuric acid; on evaporation of the solution, 12-tungstophosphoric acid first separates, and from the mother-liquor hexagonal crystals of 21 : 2-tungstophosphoric acid can then be obtained. The acid is readily soluble in water. The hydrogen-ion concentration in a 0.005 N solution<sup>6</sup> is  $7.0 \times 10^{-3}$ . Its composition may be represented by the formula  $3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 21\text{WO}_3 \cdot 55\text{H}_2\text{O}$ , indicating a hexabasic acid, and the salts prepared have the composition  $3\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 21\text{WO}_3 \cdot x\text{H}_2\text{O}$ . These, however, appear to be acid

<sup>1</sup> Sprenger, *loc. cit.*; Kehrman and Freinkel, *Ber.*, 1891, 24, 2326; 1892, 25, 1966; *Zeitsch. anorg. Chem.*, 1892, 1, 423; Gibbs, *Amer. Chem. J.*, 1880, 2, 217; Rosenheim and Jänike, *Zeitsch. anorg. Chem.*, 1917, 101, 235.

<sup>2</sup> Rosenheim and Jänike, *loc. cit.*

<sup>3</sup> Kehrman and Freinkel, *loc. cit.*

<sup>4</sup> Gibbs, *loc. cit.*

<sup>5</sup> Kehrman, *Ber.*, 1891, 24, 2335; 1892, 25, 1969; *Zeitsch. anorg. Chem.*, 1892, 1, 437; Rosenheim and Jänike, *ibid.*, 1917, 101, 258.

<sup>6</sup> Brauer, *loc. cit.*

salts, their solutions containing hydrogen ions, so that the acid may have a higher basicity than six. This view is supported by conductivity measurements; for example, in the case of the potassium salt at 25° C. the following are the equivalent conductivity values for solutions containing  $\frac{1}{6}$  molecule in  $\tau$  litres: <sup>1</sup>

$\nu =$ 32	64	128	256	512	1024
$\Lambda =$ 166.8	184.2	202.2	226.3	254.1	285.2.

Normal salts of this series have not been prepared, so that the constitution of the acid cannot yet be expressed.

The *potassium salt*,  $3K_2O \cdot P_2O_5 \cdot 21WO_3 \cdot 31H_2O$ , may be prepared by treating a solution of potassium 11-tungstophosphate with excess of dilute hydrochloric acid and boiling the mixture. Potassium 12-tungstophosphate is precipitated and separated by filtration, and on standing the filtrate slowly deposits transparent prismatic crystals of the 21 : 2-tungstophosphate.<sup>2</sup> This salt may also be prepared by the addition of potassium chloride to a solution of the free acid.<sup>3</sup> The corresponding *ammonium salt* is obtained by treating a solution of the potassium salt or of the free acid with ammonium chloride. The addition of silver nitrate to a solution of the potassium salt yields the silver salt.

**10-Tungstophosphoric Acid**, ( $P_2O_5 : WO_3$  1 : 20), and corresponding salts have been described by several authors,<sup>4</sup> but their existence is open to doubt. From the properties of the compounds described, and the methods used for their preparation, it would appear probable that they are identical with the 12-tungstophosphates.

**9-Tungstophosphoric Acid**, ( $P_2O_5 : WO_3$  1 : 18), luteophosphotungstic acid, is formed by treating the 12- or 11-tungstophosphoric acid solutions with excess of phosphoric acid. It may best be prepared from its salts, for example, by treating the ammonium salt with aqua regia, or by decomposing the silver salt with hydrochloric acid.<sup>5</sup> A colourless solution is obtained, which on evaporation turns yellow, and lemon-yellow hexagonal crystals separate. These melt at 28° C. and are very soluble in water. The acid probably exists in two isomeric forms.<sup>6</sup> Its composition is represented by the formula  $P_2O_5 \cdot 18WO_3 \cdot 42H_2O$ , and its basicity appears to be 10 (see below), so that the constitutional formula



has been suggested.<sup>3</sup> In this case an inner bridge connects the two nuclei. This is supported by conductivity measurements and a study of the neutralisation curves. The corresponding molybdo-phosphoric acid is 12-basic (see p. 165), but the complex ion in that acid is not so stable as the tungstic ion. The hydrogen-ion concentration in a 0.005 N solution of 9-tungstophosphoric acid <sup>1</sup> is  $4.1 \times 10^{-3}$ .

Salts of this acid may be prepared by boiling a mixture containing normal sodium tungstate,  $Na_2WO_4 \cdot 2H_2O$  (2 parts), syrupy phosphoric acid (3 parts), and water (1 part). The solution turns yellow, and on

<sup>1</sup> Brauer, *Dissertation*, Berlin, 1918.

<sup>2</sup> Kehrman and Freinkel, *Ber.*, 1892, 25, 1966.

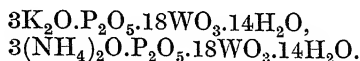
<sup>3</sup> Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1917, 101, 258.

<sup>4</sup> Péchard, *Compt. rend.*, 1889, 109, 301; *Ann. Chim. Phys.*, 1891, [6], 22, 231; Gibbs, *Amer. Chem. J.*, 1895, 17, 183; Groth, *Chemische Kristallographie*, 1906, i., 133.

<sup>5</sup> Kehrman, *Zeitsch. anorg. Chem.*, 1893, 4, 138.

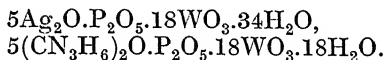
<sup>6</sup> Wu, *J. Biol. Chem.*, 1920, 43, 189.

evaporation and cooling, greenish-yellow plates consisting of a mixture of sodium salts separate.<sup>1</sup> If, instead of permitting crystallisation, the mixture is oxidised with a few drops of concentrated nitric acid, allowed to cool, and solid potassium or ammonium chloride added, yellow triclinic prisms of the potassium or ammonium salt separate. These may be purified by repeated crystallisation. They are readily soluble in water, and have composition



These salts, as well as the corresponding sodium and barium salts, may also be obtained by treating the free acid with the corresponding carbonate or chloride. The silver salt,  $3\text{Ag}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 16\text{H}_2\text{O}$ , is prepared by treating a solution of the potassium salt with silver nitrate.

These acid salts correspond to the acid salts of 9-molybdo-phosphoric acid. The following salts, which show a basicity of 10, and appear to be the normal salts of the acid, have also been prepared : <sup>2</sup>



The silver salt is obtained by treating a 30 per cent. solution of the acid with 5 to 6 molecular proportions of sodium hydroxide, and adding a soluble silver salt. A yellow flaky precipitate results which is almost insoluble in water. The guanidine salt is produced similarly, and yields bright yellow aggregates of small tables which are only slightly soluble in water.

**17 : 2-Tungstophosphates, ( $\text{P}_2\text{O}_5 : \text{WO}_3 = 1 : 17$ ).**<sup>3</sup>—By carefully neutralising a solution of 9-tungstophosphoric acid, or by treating a solution of an alkali 9-tungstophosphate with the corresponding alkali hydrogen carbonate, salts of this series are obtained. The potassium salt,  $5\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17\text{WO}_3 \cdot 22\text{H}_2\text{O}$ , yields white satiny needles. The ammonium salt,  $5(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17\text{WO}_3 \cdot 16\text{H}_2\text{O}$ , forms tabular crystals. A silver salt, of composition  $5\text{Ag}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17\text{WO}_3 \cdot 20\text{H}_2\text{O}$ , is obtained in small tabular crystals by double decomposition. The constitution of these salts is not yet determined.

Other series containing less tungstic acid have also been described; for example, 6-tungstophosphoric acid and its salts,  $2\text{R}'_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$ ,<sup>4</sup> and 7 : 2-tungstophosphates,  $3\text{R}'_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 7\text{WO}_3 \cdot x\text{H}_2\text{O}$ .<sup>5</sup> The work on these series is, however, inconclusive.

**3-Tungstophosphates, ( $\text{P}_2\text{O}_5 : \text{WO}_3 = 1 : 6$ ).**—From a concentrated solution containing sodium tungstate and phosphate, made faintly acid with acetic acid and allowed to stand for a few days, a mass of crystals, containing two salts, separates.<sup>6</sup> On washing with

<sup>1</sup> Kehrman, *Ber.*, 1887, 20, 1805.

<sup>2</sup> Rosenheim and Jänicke, *loc. cit.*

<sup>3</sup> Kehrman, *Ber.*, 1887, 20, 1806, 1810; *Annalen*, 1888, 245, 43; *Zeitsch. anorg. Chem.*, 1893, 4, 138; 1894, 6, 386; Rosenheim and Jänicke, *ibid.*, 1917, 101, 261. This series was at first regarded by Kehrman as the 8-tungstophosphates, ( $\text{P}_2\text{O}_5 : \text{WO}_3 = 1 : 16$ ).

<sup>4</sup> Péchard, *Compt. rend.*, 1889, 109, 301; 1890, 110, 754; *Ann. Chim. Phys.*, 1891, [6], 22, 248; Dufet, *Bull. Soc. franç. Min.*, 1890, 13, 202; Kehrman, *Zeitsch. anorg. Chem.*, 1892, 1, 438.

<sup>5</sup> Kehrman and Mellet, *Helv. Chim. Acta*, 1922, 5, 942; Scheibler, *Ber.*, 1872, 5, 801.

<sup>6</sup> Kehrman and Mellet, *loc. cit.*

water, the sodium salt of this series,  $3\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 6\text{WO}_3 \cdot \text{aq.}$ , dissolves, leaving a very sparingly soluble salt, the composition of which appears to be  $14\text{Na}_2\text{O} \cdot 5\text{P}_2\text{O}_5 \cdot 19\text{WO}_3 \cdot \text{aq.}$ , or  $29\text{Na}_2\text{O} \cdot 10\text{P}_2\text{O}_5 \cdot 39\text{WO}_3 \cdot \text{aq.}$

The soluble sodium 3-tungstophosphate may be obtained pure by repeated recrystallisation,<sup>1</sup> and yields aggregates of white striated prisms of composition  $3\text{Na}_2\text{O} \cdot 3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 6\text{WO}_3 \cdot 13\text{H}_2\text{O}$ . As this formula indicates, 3 molecules of water appear to be firmly held as water of constitution. The corresponding potassium and ammonium salts,  $3\text{K}_2\text{O} \cdot 3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 6\text{WO}_3 \cdot 11\text{H}_2\text{O}$  and  $3(\text{NH}_4)_2\text{O} \cdot 3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 6\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , are prepared by adding potassium or ammonium chloride to a solution of the sodium salt, than which they are much less soluble. The former yields brilliant prismatic needles, the latter short stout prisms. The free acid has not been prepared.

**Hypophosphotungstates.**<sup>2</sup> The potassium salt,  $4\text{K}_2\text{O} \cdot 6\text{H}_3\text{PO}_2 \cdot 18\text{WO}_3 \cdot 7\text{H}_2\text{O}$ , has been described, but its existence has not been confirmed.

### TUNGSTEN AND ARSENIC.

**Tungsten Diarsenide,  $\text{WAs}_2$ ,** is prepared<sup>3</sup> by heating pure tungsten hexachloride in a current of hydrogen arsenide, the temperature being maintained at  $150^\circ$  to  $200^\circ \text{C.}$  for a time and then gradually raised to  $350^\circ \text{C.}$  The arsenide remains as a black crystalline mass, of density 6.9 at  $18^\circ \text{C.}$  It is stable in air at ordinary temperature; at red heat it is readily oxidised, leaving a residue of yellow tungstic anhydride. It readily combines with chlorine, sulphur, and phosphorus when heated. It is quite insoluble in water, carbon disulphide, and the usual organic solvents; solutions of hydrofluoric and hydrochloric acids have no action upon it, but nitric acid and aqua regia oxidise it on warming. Fused alkalis and alkali carbonates act upon it to form arsenate and tungstate.

**Tungsten Chloro-arsenide,  $\text{W}_2\text{AsCl}_9$ ,** is obtained by heating a mixture of tungsten hexachloride and liquid hydrogen arsenide in a sealed tube at  $60^\circ$  to  $75^\circ \text{C.}$ <sup>4</sup> The substance forms bluish-black, hygroscopic crystals, resembling the hexachloride. It is readily decomposed by water, acids, and alkalis.

**Arsenotungstic Acids and Arsenotungstates.** These compounds are analogous to the phosphotungstic acids and their salts, but the complex anions are essentially more unstable than those of the phosphorus compounds. The investigation of these acids and salts is as yet very incomplete.<sup>5</sup>

**12-Tungsto-arsenates.** Only the ammonium salt,  $(\text{NH}_4)_3\text{H}_4[\text{As}(\text{W}_2\text{O}_7)_6] \cdot 11\text{H}_2\text{O}$ , has been prepared.<sup>6</sup> It separates as a white crystalline precipitate when a solution containing normal sodium tungstate

<sup>1</sup> Kehrman and Mellet, *Helv. Chim. Acta*, 1923, 6, 443, 656.

<sup>2</sup> Gibbs, *Amer. Chem. J.*, 1884, 5, 361; *Bull. Soc. chim.*, 1884, 41, 618, 625. See also *Proc. Amer. Acad.*, 1885, 21, 110; *Br.*, 1885, 18, 1089.

<sup>3</sup> Defacqz, *Compt. rend.*, 1901, 132, 138.

<sup>4</sup> Defacqz, *loc. cit.*; *Ann. Chim. Phys.*, 1901, [7], 22, 238.

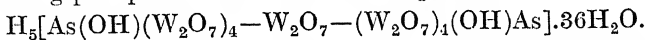
<sup>5</sup> See Gibbs, *Br.*, 1878, 10, 1384; *Proc. Amer. Acad.*, 1880, 16, 134; *Amer. Chem. J.*, 1885-86, 7, 313; Lefort, *Compt. rend.*, 1881, 92, 1461; *Ann. Chim. Phys.*, 1882, [5], 25, 200; Fremery, *Br.*, 1884, 17, 296; *Bull. Soc. chim.*, 1884, 42, 457; Kehrman, *Annalen*, 1888, 245, 52; *Bull. Soc. chim.*, 1889, [3], 2, 19; *Zeitsch. anorg. Chem.*, 1900, 22, 290; Sweeney, *J. Amer. Chem. Soc.*, 1916, 38, 2377.

<sup>6</sup> Rosenheim and Jänecke, *Zeitsch. anorg. Chem.*, 1917, 101, 235.

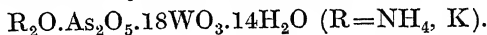
(8 molecules) and arsenic acid (1 molecule) is acidified with hydrochloric acid, treated with solid ammonium chloride, and boiled. The free acid is unstable and undergoes hydrolysis in solution.

**11-Tungsto-arsenates.**—These are completely analogous to the 11-tungstophosphates. The *barium salt*,  $7\text{BaO} \cdot \text{As}_2\text{O}_5 \cdot 22\text{WO}_3 \cdot 54\text{H}_2\text{O}$  or  $\text{Ba}_7[\text{As}(\text{OH})(\text{W}_2\text{O}_7)_5] - \text{W}_2\text{O}_7 - [(\text{W}_2\text{O}_7)_5(\text{OH})\text{As}] \cdot 53\text{H}_2\text{O}$ , is obtained by adding a 5 per cent. solution of ammonium carbonate to a suspension of the ammonium 12-tungsto-arsenate in boiling water until a clear solution results, when, on adding barium chloride, the salt crystallises in double pyramids isomorphous with the corresponding phosphate. Other salts of the series may be obtained from the barium salt by double decomposition.

**9-Tungsto-arsenic Acid**, luteo-arsenotungstic acid, may be obtained by saturation of a boiling solution of an alkali arsenate with tungstic anhydride, and allowing the mixture to stand for several weeks until the reactions of the 12-tungsto-arsenate have disappeared; or by acidifying a solution of one of its salts and shaking out with ether according to Drechsel (see p. 251). The acid is isomorphous with the corresponding phosphoric acid and has composition



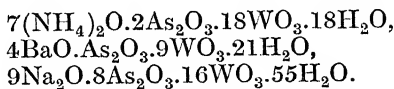
It melts at  $26^\circ \text{C}$ . Only the ammonium and potassium salts of this series have been prepared. These are obtained by adding arsenic acid to a boiling solution of alkali tungstate until the colour becomes deep yellow, and then treating with ammonium or potassium chloride. On evaporation the solution yields lemon-yellow crystals of composition



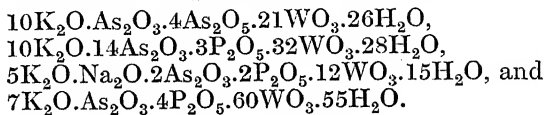
**17 : 2-Tungsto-arsenates.**—Solutions of the 9-tungsto-arsenates, when treated with the corresponding carbonates until the yellow colour disappears, yield colourless crystalline precipitates of salts belonging to this series, isomorphous with the corresponding phosphates and of composition  $5(\text{NH}_4)_2\text{O} \cdot \text{As}_2\text{O}_5 \cdot 17\text{WO}_3 \cdot 16\text{H}_2\text{O}$  and  $5\text{K}_2\text{O} \cdot \text{As}_2\text{O}_5 \cdot 17\text{WO}_3 \cdot 22\text{H}_2\text{O}$ .

**Alumino-arsenotungstates**, see p. 211.

**Tungsto-arsenites.**—By treating solutions of tungstates with arsenious acid the following crystalline compounds have been obtained by Gibbs,<sup>1</sup>



This author also describes compounds of composition



#### TUNGSTEN AND ANTIMONY.

By boiling a solution of potassium paratungstate with excess of antimoniac acid a solution is obtained from which crystals of a potassium antimoniotungstate, of composition  $2\text{WO}_3 \cdot 3\text{KSbO}_3 \cdot 8\text{H}_2\text{O}$ , may be

<sup>1</sup> Gibbs, *Amer. Chem. J.*, 1885, 7, 317.



obtained.<sup>1</sup> The corresponding silver salt, treated with hydrochloric acid and the solution evaporated in a vacuum, yields a vitreous residue of the acid,  $4\text{WO}_3 \cdot 3\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O} + 8\text{H}_2\text{O}$ . A barium salt of composition  $2\text{BaO} \cdot 3\text{Sb}_2\text{O}_5 \cdot 11\text{WO}_3 \cdot 18\text{H}_2\text{O}$  is described by Gibbs.<sup>2</sup>

**Antimony Tungstate**, see p. 213.

**Alumino-antimoniotungstates**, see p. 211.

#### TUNGSTEN AND BISMUTH.

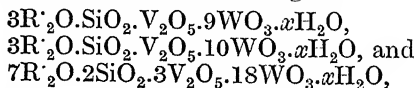
Several complex bismuthotungstates, of the type  $3\text{R}'_2\text{O} \cdot 2\text{Bi}_2\text{O}_3 \cdot 11\text{WO}_3 \cdot x\text{H}_2\text{O}$ , have been obtained.<sup>3</sup> The salts of potassium, ammonium, and strontium are oily substances which when dried yield yellow vitreous masses. By treating the potassium salt with a mercurous salt a yellow, well-defined, and stable bismuthotungstate, of composition  $3\text{Hg}_2\text{O} \cdot 2\text{Bi}_2\text{O}_3 \cdot 11\text{WO}_3 \cdot 15\text{H}_2\text{O}$ , is obtained.<sup>4</sup> By the action of hydrochloric acid on this substance a greenish-yellow solid of the formula  $2\text{Bi}_2\text{O}_3 \cdot 6\text{HCl} \cdot 11\text{WO}_3$  may be isolated.

**Bismuth Tungstate**, see p. 215.

#### TUNGSTEN AND VANADIUM.

Three well-defined series of complex salts containing tungsten and vanadium have been prepared.<sup>5</sup> They are obtained (1) by saturation of a solution of a paratungstate with vanadium pentoxide, (2) by the action of acetic acid on solutions of mixed alkali tungstates and vanadates, or (3) by the addition of a paratungstate to a metavanadate. The salts are characteristically coloured and all contain water of constitution. The dichromate coloured series have composition  $5\text{R}'_2\text{O} \cdot 0.3\text{V}_2\text{O}_5 \cdot 6\text{WO}_3 \cdot x\text{H}_2\text{O}$  ( $\text{R}' = \text{NH}_4, \text{K}, \text{Na}$ ). The yellowish-red salts have composition  $2\text{R}'_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 4\text{WO}_3 \cdot x\text{H}_2\text{O}$ , and salts of the alkali metals, alkaline earth metals, and silver have been prepared. The salts of both these series have properties similar to the paratungstates. The salts of the third series are deep red in colour, of composition  $5\text{R}'_2\text{O} \cdot 0.3\text{V}_2\text{O}_5 \cdot 14\text{WO}_3 \cdot x\text{H}_2\text{O}$ , and resemble the metatungstates. The ammonium, potassium, caesium, and barium salts have been prepared.

More complex compounds have also been prepared; for example, an ammonium phosphovanadotungstate,  $13(\text{NH}_4)_2\text{O} \cdot 0.2\text{P}_2\text{O}_5 \cdot 8\text{V}_2\text{O}_5 \cdot 34\text{WO}_3 \cdot 86\text{H}_2\text{O}$ ; <sup>6</sup> corresponding potassium and barium salts have also been prepared. Three series of silico-vanadotungstates of composition



have been described.<sup>7</sup>

<sup>1</sup> Hallopeau, *Compt. rend.*, 1896, 123, 1065.

<sup>2</sup> Gibbs, *Amer. Chem. J.*, 1885, 7, 317.

<sup>3</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1903, 25, 1229.

<sup>4</sup> Sweeney, *ibid.*, 1916, 38, 2377.

<sup>5</sup> Rammelsberg, *Ber.*, 1868, 1, 161; Gibbs, *Amer. Chem. J.*, 1886, 5, 361; Ditte, *Compt. rend.*, 1886, 102, 1019; Rosenheim, *Annalen*, 1889, 251, 197; Friedheim, *Ber.*, 1890, 23, 1505; Rothenbach, *ibid.*, 1890, 23, 3050; Friedheim and Löwy, *Zeitsch. anorg. Chem.*, 1894, 6, 11; Prandtl and Hecht, *ibid.*, 1915, 92, 198; Sweeney, *loc. cit.*; Rosenheim and Pieck, *Zeitsch. anorg. Chem.*, 1916, 98, 223.

<sup>6</sup> Rogers, *J. Amer. Chem. Soc.*, 1903, 25, 298, 1223, 1227. See also Gibbs, *Amer. Chem. J.*, 1883, 5, 395.

<sup>7</sup> Friedheim and Castendyck, *Ber.*, 1900, 33, 1611; Friedheim and Henderson, *ibid.*, 1902, 35, 3242.

## TUNGSTEN AND CARBON.

When metallic tungsten is heated with carbon in an electric furnace carbide formation takes place, and the carbides  $W_3C$ ,  $WC$ , and probably  $W_2C$  appear capable of existence.<sup>1</sup> A carbide of composition  $W_3C_4$  has also been described<sup>2</sup> as being formed when finely powdered tungsten is heated in carbon monoxide at  $1000^\circ C.$ , but its existence as a chemical entity is doubted by Ruff.<sup>3</sup>

**Tritungsten Carbide,  $W_3C$ ,** melts above  $2700^\circ C.$ , and solidifies as a homogeneous substance. It does not form solid solutions with tungsten to any considerable extent, as a separate constituent may be detected when the carbon reaches only 0.12 per cent.

**Ditungsten Carbide,  $W_2C$ ,** was described by Moissan<sup>4</sup> as an iron-grey mass, produced by heating an intimate mixture of tungstic anhydride and carbon in an electric furnace. The product was harder than corundum, of density 16.06 at  $18^\circ C.$ , and was very similar in properties to the metal itself. According to Ruff and Wunsch, this product was not a pure carbide; in their own investigation they detected a micrographic constituent between the mono- and tri-tungsten carbides, but were unable to definitely determine its composition.

**Tungsten Monocarbide,  $WC$ ,** is obtained by heating a mixture of tungstic anhydride and carbon, in presence of a large excess of iron, in an electric furnace,<sup>5</sup> or by heating finely powdered tungsten, or the anhydride, at  $800^\circ C.$  in an atmosphere of methane and hydrogen (1 : 1).<sup>2</sup> It is a dark grey, crystalline powder, of density 15.7 at  $18^\circ C.$ , and is harder than quartz. When heated strongly it decomposes, yielding graphite and lower carbides; whilst in presence of air it forms tungstic anhydride and carbon dioxide.

**Tungsten Iron Carbides.**—By heating a mixture of tungstic anhydride, iron, and petroleum coke in a carbon crucible in an electric furnace a double carbide is formed, for which the formula  $2Fe_3C.3W_2C$  has been suggested.<sup>6</sup> The carbide is highly magnetic and may be separated by means of a magnet after treatment of the product with hot concentrated hydrochloric acid. It is obtained in brilliant microscopic prisms with the colour of pyrites and of density 13.4 at  $18^\circ C.$  A double carbide, of composition  $Fe_3C.WC$ , has also been obtained by the action of dilute acid on tungsten steel.<sup>7</sup> This is the normal condition in which tungsten carbide is present in steel. The double carbide decomposes at  $400^\circ C.$

Tungsten chromium carbide, see p. 94.

## TUNGSTEN AND CYANOGEN.

Simple cyanides of tungsten have not been isolated, but two well-defined series of complex cyanides are known, one containing tetra-

<sup>1</sup> Ruff and Wunsch, *Zeitsch. anorg. Chem.*, 1914, 85, 292.

<sup>2</sup> Hilpert and Ornstein, *Ber.*, 1913, 46, 1669.

<sup>3</sup> Abegg-Auerbach, *Handbuch der anorganischen Chemie*, Leipzig, 1921, iv., 1, 2 Halbbd., p. 849.

<sup>4</sup> Moissan, *Compt. rend.*, 1896, 123, 13; *Ann. Chim. Phys.*, 1896, [7], 8, 570.

<sup>5</sup> Williams, *Compt. rend.*, 1898, 126, 1722.

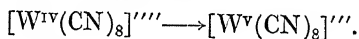
<sup>6</sup> Williams, *ibid.*, 1898, 127, 410.

<sup>7</sup> Carnot and Goutal, *ibid.*, 1899, 128, 207. See also Daewes, *Zeitsch. anorg. Chem.*, 1921, 118, 67; Honda and Murakami, *Sci. Rep. Tohoku Imp. Univ.*, 1918, 6, 235; Ozawa, *ibid.*, 1922, 11, 333.

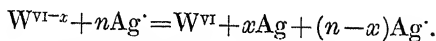
valent tungsten and of composition  $R'_4[W(CN)_8]$ , the other with pentavalent tungsten and general formula  $R'_3[W(CN)_8]$ .

**Tungstocyanic Acid**,  $H_4[W(CN)_8] \cdot 6H_2O$ , may be prepared<sup>1</sup> by treating the silver salt with a slight excess of cold dilute hydrochloric acid, and saturating the clear filtrate with hydrogen chloride below  $0^\circ C$ . The acid separates in yellow needles, and may be dried first in carbon dioxide and then in a desiccator over potassium hydroxide. It may also be obtained by the action of concentrated acid in the cold on the potassium salt.<sup>2</sup> The product, which is soluble in water and in alcohol, is a strong acid and readily decomposes carbonates. The crystals deliquesce in moist air; if dried over sulphuric acid, they lose about three-fourths of their water content. When heated above  $60^\circ C$ . they decompose.

The salts of this acid are analogous to the corresponding molybdocyanides (see p. 172). Those of the alkali and alkaline earth metals are soluble in water, those of the heavier metals are insoluble, and all are insoluble in ordinary organic solvents. Many of the cyanides—for example, those of cadmium, copper, nickel, silver, and zinc—dissolve in concentrated ammonia solutions and yield, on recrystallisation, metal ammine derivatives.<sup>1</sup> The tungstocyanides, which are generally yellow in colour, yield yellow neutral solutions which are generally stable and are unaffected by dilute acids or alkalis. Hot dilute nitric acid causes slight oxidation, whilst hot concentrated nitric or sulphuric acid causes complete decomposition. In dilute sulphuric acid solution the compounds of this series are oxidised by potassium permanganate in such a way that for each tungsten atom present one half atom of oxygen is used up. This fact appeared to contradict the presence of tetravalent tungsten, since in the usual course of oxidation, *i.e.* in passing from  $W^{IV}$  to  $W^{VI}$ , one atom of tungsten requires one atom of oxygen. However, investigation<sup>3</sup> confirmed the tetravalency of tungsten, the product of oxidation being not tungstic acid, but a complex cyanide, containing pentavalent tungsten, of the type  $R'_3[W(CN)_8]$ . The transformation of the anion may therefore be expressed



The valency of the tungsten in both these series of compounds is further confirmed by determining the amount of silver deposited on heating them for ten to twelve hours at  $140^\circ$  to  $160^\circ C$ . with ammoniacal silver nitrate in a sealed tube.<sup>4</sup> The reaction takes place according to the equation



**Ammonium Tungstocyanide**,  $(NH_4)_4[W(CN)_8]$ , is prepared by neutralisation of the free acid by means of ammonia. It crystallises in lustrous scales without water of crystallisation. If heated above  $60^\circ C$ . decomposition occurs.

**Calcium Tungstocyanide**,  $Ca_2[W(CN)_8] \cdot 8H_2O$ , is formed by the action of calcium chloride on the silver salt. It is easily soluble in

<sup>1</sup> Olsson, *Zeitsch. anorg. Chem.*, 1914, 88, 49.

<sup>2</sup> Rosenheim and Dehn, *Ber.*, 1915, 48, 1167.

<sup>3</sup> Olsson, *ibid.*, 1914, 47, 917; Rosenheim and Dehn, *loc. cit.*; Dehn, *Dissertation*, Berlin, 1915.

<sup>4</sup> Olsson, *loc. cit.*; Rosenheim and Dehn, *loc. cit.*; Collenberg, *Zeitsch. anorg. Chem.*, 1922, 121, 298.

water. On heating to  $115^{\circ}$  C. the crystals lose all their water of crystallisation.

**Cadmium Tungstocyanide**,  $\text{Cd}_2[\text{W}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ , may be prepared from the silver salt by double decomposition,<sup>1</sup> or by the following method due to Rosenheim and Dehn.<sup>2</sup> A solution of 12-tungstosilicic acid (see p. 264) in concentrated hydrochloric acid is reduced electrolytically<sup>3</sup> until the solution becomes greenish yellow in colour. Strong alkali is added to remove the excess of acid, and solid potassium cyanide is then added in considerable quantity. On evaporation of this solution, potassium chloride separates. A similar solution may be obtained more directly by treating the compound  $\text{K}_3\text{W}_2\text{Cl}_9$  (see p. 195) with potassium cyanide.<sup>4</sup> The solution is now treated with a concentrated solution of cadmium sulphate and digested on the water-bath; an impure cadmium salt separates which is dissolved in concentrated ammonia solution, and the solution, placed in a freezing mixture, is saturated with ammonia. *Cadmiumtriammine tungstocyanide*,  $[\text{Cd}(\text{NH}_3)_3]_2[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ , separates in long golden-yellow needles, which on washing with water, or on exposure to air, lose ammonia and yield the corresponding diammine salt,  $[\text{Cd}(\text{NH}_3)_2]_2[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ . On treatment with 1 to 2 per cent. sulphuric acid, microscopic yellow prisms of cadmium tungstocyanide,  $\text{Cd}_2[\text{W}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ , are obtained. When exposed to sunlight the crystals turn red but no change in weight occurs, and on heating, the yellow colour returns. When heated to  $125^{\circ}$  C. 7 molecules of water are lost. The salt is only slightly soluble in water, but is more readily soluble in hydrochloric acid.

The cadmium salt may also be obtained from the pyridine compound  $\text{W}(\text{OH})_2(\text{SCN})_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ , which dissolves in potassium cyanide solution, forming a blue solution which turns yellow on warming and can be made to yield the above-mentioned triammine salt.<sup>5</sup>

**Cæsium Tungstocyanide**,  $\text{Cs}_4[\text{W}(\text{CN})_8]$ , may be prepared by neutralisation of the free acid with cæsium carbonate. It yields light yellow, easily soluble crystals.

**Lead Tungstocyanide**,  $\text{Pb}_2[\text{W}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ , is obtained by the action of lead chloride on the silver salt; on adding alcohol, lustrous yellow needles separate. These, when heated to  $115^{\circ}$  C., lose their water of crystallisation.

**Magnesium Tungstocyanide**,  $\text{Mg}_2[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$ , is prepared from the silver salt by the addition of magnesium chloride. It is readily soluble in water; the solution, on heating, decomposes.

**Manganese Tungstocyanide**,  $\text{Mn}_2[\text{W}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ , is obtained by precipitation when a manganese salt is added to a solution of potassium tungstocyanide. It is insoluble in water and acids. On heating, it loses at  $130^{\circ}$  C. 7 molecules of water, and at  $140^{\circ}$  C. begins to decompose.

**Potassium Tungstocyanide**,  $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ , may be prepared by the action of potassium carbonate on the cadmium salt, or by treating a solution of potassium tungsten chloride,  $\text{K}_3\text{W}_2\text{Cl}_9$ , with potassium cyanide. It yields light yellow microscopic prisms, which

<sup>1</sup> Olsson, *loc. cit.*

<sup>2</sup> Rosenheim and Dehn, *Ber.*, 1914, 47, 392.

<sup>3</sup> See Rosenheim and Loebel, *Zeitsch. anorg. Chem.*, 1908, 57, 234.

<sup>4</sup> Olsson, *loc. cit.*; *Zeitsch. anorg. Chem.*, 1914, 88, 49.

<sup>5</sup> Rosenheim and Dehn, *Ber.*, 1915, 48, 1167.

lose all their water at  $115^{\circ}\text{C}$ . According to Olsson,<sup>1</sup> 10 c.c. of water dissolve 13 to 14 grams of the salt at  $18^{\circ}\text{C}$ . The electrical conductivities of solutions containing one equivalent in  $v$  litres at  $25^{\circ}\text{C}$ . have been determined as follows: <sup>2</sup>

$v = 32$	64	128	256	512	1024
$\Lambda = 118.8$	130.0	140.6	149.5	159.8	165.8.

**Rubidium Tungstocyanide**,  $\text{Rb}_4[\text{W}(\text{CN})_8] \cdot 3\text{H}_2\text{O}$ , from the silver salt and rubidium chloride, yields small pale yellow crystals, less soluble than the potassium salt. It loses all its water at  $110^{\circ}\text{C}$ .

**Silver Tungstocyanide**,  $\text{Ag}_4[\text{W}(\text{CN})_8]$ , is obtained as a yellow amorphous powder by adding a silver salt to a solution of the potassium tungstocyanide. It is quite insoluble in water and acids, but readily reacts with metallic chlorides with double decomposition. It is decomposed by sunlight. It dissolves in concentrated ammonia solution, forming the ammine salt,  $[\text{AgNH}_3]_4[\text{W}(\text{CN})_8]$ , which separates, on cooling, as bright yellow crystals. This compound is stable in an atmosphere of ammonia and in the dark, but in air it loses ammonia and in sunlight turns yellowish red.

**Sodium Tungstocyanide**,  $2\text{Na}_4[\text{W}(\text{CN})_8] \cdot 5\text{H}_2\text{O}$ , may be obtained by neutralisation of the free acid with sodium hydroxide, or by double decomposition from the silver salt and sodium chloride. It yields small yellow deliquescent crystals.

**Strontium Tungstocyanide**,  $\text{Sr}_2[\text{W}(\text{CN})_8] \cdot 8$  or  $9\text{H}_2\text{O}$ , is obtained from the silver salt by double decomposition.

**Thallium Tungstocyanide**,  $\text{Tl}_4[\text{W}(\text{CN})_8]$ , is obtained by double decomposition from potassium tungstocyanide and a thallium salt. It forms long yellow needles which become red in sunlight but regain their yellow colour when heated. The salt is only sparingly soluble in cold water, but more readily soluble in hot.

**Zinc Tungstocyanide**,  $\text{Zn}_2[\text{W}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ , is prepared by precipitation from a solution of the potassium salt. It is insoluble in water and acids. When heated, it loses all its water at  $130^{\circ}\text{C}$ . It dissolves in a hot solution of ammonia, forming the ammine salt,  $[\text{Zn}(\text{NH}_3)_2]_2[\text{W}(\text{CN})_8]$ , which separates on cooling. This compound loses all its ammonia on exposure to air.

Besides the salts described above, many other metals—for example, iron, mercury, copper, cobalt, and nickel—yield precipitates with soluble tungstocyanides, which, however, have not yet been fully investigated. Aluminium, bismuth, and tin ( $\text{Sn}^{++}$ ) do not yield such precipitates.

**Tungsticyanic Acid**,  $\text{H}_3[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$ , is obtained from its silver salt by the action of hydrochloric acid.<sup>3</sup> It forms orange-yellow crystals which over sulphuric acid turn reddish brown, with loss of water. It is unstable, and decomposes in daylight and in moist air. As has already been mentioned (see p. 260), the compounds of this series are not oxidised by potassium permanganate, although the tungsten is only pentavalent, as is shown by the liberation of silver from ammoniacal silver nitrate.

The potassium salt,  $2\text{K}_3[\text{W}(\text{CN})_8] \cdot 5\text{H}_2\text{O}$ , is obtained<sup>3</sup> by oxidising a solution of the tungstocyanide,  $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ , with

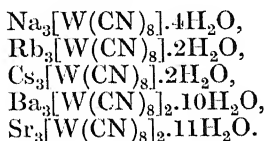
<sup>1</sup> Olsson, *Ber.*, 1914, 47, 917; *Zeitsch. anorg. Chem.*, 1914, 88, 49.

<sup>2</sup> Rosenheim and Dehn, *Ber.*, 1915, 48, 1167.

<sup>3</sup> Olsson, *Ber.*, 1914, 47, 917.

potassium permanganate, adding silver nitrate, which precipitates the red silver tungsticyanide, and treating this with a solution of potassium chloride. The silver chloride is removed by filtration, and the solution on evaporation yields light yellow crystals of the potassium salt. The crystals are fairly stable in dry air, but undergo decomposition when exposed to moist air in daylight. The salt readily forms additive products; for example, with potassium chloride it yields red slender prisms of composition  $K_3[W(CN)_8] \cdot KCl \cdot 5H_2O$ .

The following salts have also been obtained by the action of the metallic chlorides on the silver salt: <sup>1</sup>



Thiocyanates of tungsten have not been prepared. Complex salts containing pyridine and of composition  $(C_5H_5NH)_2.WO(SCN)_5 \cdot xH_2O$ ,<sup>2</sup>  $(C_5H_5N)_2.W(OH)_2(SCN)_3$ ,<sup>3</sup> and  $2(C_5H_5N.HCNS).WO_2(SCN)_4$  have been isolated.

Various complex compounds of tungstic acid with organic acids, such as oxalic, tartaric, citric, malic, and lactic acids, have been described.<sup>5</sup>

#### TUNGSTEN AND SILICON.

Three silicides of tungsten, of composition  $W_2Si_3$ ,  $WSi_2$ , and  $WSi_3$ , have been isolated.

**Tungsten Sesquisilicide,  $W_2Si_3$ ,** is obtained by heating a mixture, containing 10 parts of silicon and 23 parts of tungstic anhydride, in an electric furnace.<sup>6</sup> The product is suspended in dilute hydrochloric acid, and the excess of free tungsten removed by electrolysis; the silicide collects at the bottom of the vessel and is treated successively with aqua regia, ammonia, and hydrofluoric acid, any carbon silicide present being finally removed by means of methylene iodide. It forms lustrous steel-grey plates, of density 10.9. It is fusible at red heat and readily oxidises; in oxygen it burns brilliantly at 500° C. The halogens attack it at comparatively low temperatures. On the other hand, it is very resistant to acids and alkalis in solution; aqua regia has practically no action, but a mixture of nitric and hydrofluoric acids decompose it even at ordinary temperatures, whilst fused alkali hydroxides and carbonates also attack it readily.

**Tungsten Disilicide,  $WSi_2$ ,** is obtained <sup>7</sup> by heating together copper silicide and amorphous tungsten in an electric furnace. The product is washed and treated successively with nitric acid, sodium hydroxide, warm hydrofluoric acid, and water. It may also be obtained by the aluminothermic process, by ignition of a mixture containing

<sup>1</sup> Olsson, *loc. cit.*

<sup>2</sup> Collenberg, *Zeitsch. anorg. Chem.*, 1918, 102, 247.

<sup>3</sup> Rosenheim and Dehn, *loc. cit.*

<sup>4</sup> Kalischer, *Dissertation*, Berlin, 1902.

<sup>5</sup> Collenberg, *loc. cit.*; Grossmann and Krämer, *Zeitsch. anorg. Chem.*, 1904, 41, 43;

Henderson and Prentice, *Trans. Chem. Soc.*, 1903, 83, 259.

<sup>6</sup> Moissan, *Compt. rend.*, 1896, 123, 13; Vigouroux, *ibid.*, 1898, 127, 393.

<sup>7</sup> Defacqz, *ibid.*, 1907, 144, 848; Hönigschmid, *Monatsh.*, 1907, 28, 1017.

45 grams tungstic anhydride, 180 grams silica, 250 grams sulphur, and 200 grams aluminium, the product being purified by successive treatment with hydrochloric acid, sodium hydroxide, and hydrofluoric acid. Tungsten disilicide yields lustrous, light grey prisms, probably dimorphous, of density 9.4 at 0° C. The crystals are non-magnetic and are more stable than the silicide  $W_2Si_3$ . Fluorine only attacks the disilicide when slightly heated; chlorine reacts at 450° C., yielding silicon tetrachloride and tungsten hexachloride. It may be heated in air to 900° C. without change. It is slowly oxidised when heated in a current of oxygen. It is decomposed by a mixture of nitric and hydrofluoric acids, or by fused alkalis.

**Tungsten Trisilicide,  $WSi_3$ ,** was isolated by Frilley<sup>1</sup> from a mixed iron tungsten silicide containing 9 per cent. iron, 51.6 per cent. tungsten, and 38.4 per cent. silicon by successive treatment with concentrated hydrofluoric acid, hot concentrated sodium hydroxide, and dilute hydrofluoric acid. The crystals obtained were white and lustrous, and exhibited similar chemical properties to those of the disilicide.

A method of producing the silicides by direct union has been described.<sup>2</sup> The constituents are pressed into bars, and these are subjected to resistance heating.

Methods of obtaining the mixed silicides are described by Frilley,<sup>1</sup> but these products generally contain iron silicide in considerable quantity. An aluminium tungsten silicide has also been described.<sup>3</sup>

#### TUNGSTOSILICIC ACIDS AND TUNGSTOSILICATES.

**12-Tungstosilicic Acid,  $H_8[Si(W_2O_7)_6].xH_2O$ ,** was first obtained by Marignac<sup>4</sup> by decomposing the mercurous salt by means of hydrochloric acid, and allowing the resulting solution to slowly crystallise. It is more conveniently obtained by the method of Drechsel<sup>5</sup> from concentrated aqueous solutions of its salts, by shaking out with ether after the addition of hydrochloric acid (see p. 251). At ordinary temperatures, large quadratic crystals of the 28-hydrate,  $H_8[Si(W_2O_7)_6].28H_2O$ , are obtained. When these are heated above 33° C., or when the acid is allowed to crystallise from the warm solution, the 22-hydrate,  $H_8[Si(W_2O_7)_6].22H_2O$ , which yields rhombohedral crystals, is formed. The actual transition point is 28.5° C.<sup>6</sup> The 22-hydrate melts at 53° C. A 15-hydrate,  $H_8[Si(W_2O_7)_6].15H_2O$ ,<sup>6</sup> separates in fine prisms when concentrated solutions of the acid are treated with fuming hydrochloric acid. The acid is readily soluble in water and in alcohol; it is extremely stable towards hydrolysis, and its solution may be used as a reagent for alkaloids with which it gives distinctive precipitates which are definite and stable compounds.<sup>7</sup> The hydrogen-ion concentration in a 0.05 N solution of the acid<sup>8</sup> is  $2.9 \times 10^{-3}$ .

<sup>1</sup> Frilley, *Revue de Métallurgie*, 1911, 8, 502.

<sup>2</sup> Wedekind and Pintsch, *German Patent*, 295547 (1917).

<sup>3</sup> Manchot and Kieser, *Annalen*, 1904, 337, 353.

<sup>4</sup> Marignac, *Ann. Chim. Phys.*, 1864, [4], 3, 5, 76; *Compt. rend.*, 1864, 58, 809.

<sup>5</sup> Drechsel, *Ber.*, 1887, 20, 1453.

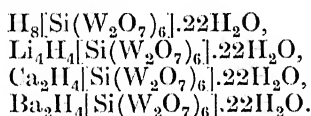
<sup>6</sup> Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1912, 77, 239; 1917, 101, 235.

<sup>7</sup> Godefroy, *Ber.*, 1876, 9, 1792; Bertrand, *Compt. rend.*, 1899, 128, 742; Bertrand and Javillier, *Bull. Soc. chim.*, 1909, [4], 5, 241; Javillier, *Chem. Zentr.*, 1912, ii., 36; Ferency and Dávid, *ibid.*, 1914, ii., 807; Taigner, *Zeitsch. anal. Chem.*, 1919, 58, 346; Guglielmelli and Hordh, *Anal. Soc. Quim. Argentina*, 1919, 7, 121; Heiduschka and Wolff, *Schweiz. Apoth.-Zeit.*, 1920, 58, 213, 229.

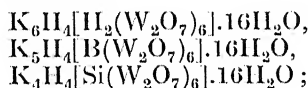
<sup>8</sup> Brauer, *Dissertation*, Berlin, 1918.

The basicity of 12-tungstosilicic acid, as indicated by the formula, appears to be 8, and normal alkali salts, for example, the *potassium salt*  $K_8[Si(W_2O_7)_6] \cdot 14H_2O$ , were described by Marignac.<sup>1</sup> Subsequent investigators,<sup>2</sup> however, could not verify Marignac's work, and showed that the products obtained by his method of preparation, namely, by saturation of solutions of the paratungstates with silicic acid gel, were salts of 10-tungstosilicic acid (see below) and not 12-tungstosilicates. The normal *mercurous salt*  $Hg_8[Si(W_2O_7)_6] \cdot 5H_2O$ , however, separates in pale yellow laminae when mercurous nitrate is added to a solution of the free acid.

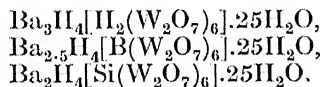
The 12-tungstosilicates usually obtained correspond to the formula  $R_4H_4[Si(W_2O_7)_6] \cdot xH_2O$ . They may be prepared by the addition of mineral acid to a boiling solution containing alkali tungstate and silicate; by the addition of alkali silicofluoride to a solution of the corresponding tungstate, until the mixture no longer yields a precipitate of tungstic acid when treated with hydrochloric acid; by treating a solution of the free acid with a metallic carbonate; or by double decomposition. The salts crystallise readily, forming well-defined crystals,<sup>3</sup> and each salt appears to form several well-defined hydrates; for example, the sodium salt  $Na_4H_4[Si(W_2O_7)_6] \cdot 18H_2O$  is dimorphous, and hydrates containing  $12H_2O$  and  $11H_2O$  respectively are also known. The copper and chromium salts each yield three hydrates. The lithium, calcium, and barium salts yield hydrates which are isomorphous with the rhombohedral form of the free acid, thus: <sup>4</sup>



Isomorphism also exists (see p. 234) between certain 12-tungstosilicates and certain metatungstates and borotungstates; for example, the following are isomorphous: <sup>5</sup>



and also <sup>6</sup>



The 12-tungstosilicates form stable double salts with nitrates; for example,  $3Na_4H_4[Si(W_2O_7)_6] \cdot 4NaNO_3 \cdot 13H_2O$  and  $Ca_2H_4[Si(W_2O_7)_6] \cdot Ca(NO_3)_2 \cdot 13H_2O$ .

The acid salts,  $Na_2H_6[Si(W_2O_7)_6] \cdot 14H_2O$  and  $K_3H_5[Si(W_2O_7)_6] \cdot 12H_2O$ , have been obtained by the action of mineral acids on the ordinary 12-tungstosilicates.

<sup>1</sup> Marignac, *loc. cit.* See also *Ann. Chim. Phys.*, 1863, [3], 69, 5; *Compt. rend.*, 1862, 55, 888; *Annalen*, 1863, 125, 362; 1864, 132, 25; *J. prakt. Chem.*, 1863, 94, 356.

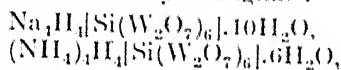
<sup>2</sup> Kehrman, *Zeitsch. anorg. Chem.*, 1904, 39, 98; Rosenheim and Jänicke, *loc. cit.*; Brauer, *loc. cit.* <sup>3</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1896, 19, 219.

<sup>4</sup> Marignac, *Ann. Chim. Phys.*, 1863, [3], 69, 38; Copaux, *Bull. Soc. franç. Min.*, 1906, 29, 77. <sup>5</sup> Copaux, *Compt. rend.*, 1909, 148, 633.

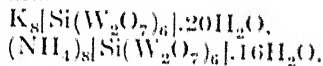
<sup>6</sup> Klein, *Ann. Chim. Phys.*, 1883, [5], 28, 392; Copaux, *Zeitsch. anorg. Chem.*, 1911, 70, 299.



**Iso-12-tungstosilicic Acid,  $H_8[Si(W_2O_7)_6] \cdot 20H_2O$ .** This compound is distinct in properties from the 12-tungstosilicic acid described above, and forms a series of salts which differ from the 12-tungstosilicates. The two isomeric forms were recognised by Marignac,<sup>1</sup> who distinguished them by the names silicotungstic acid and tungstosilicic acid. A similar isomerism occurs with the 12-tungstoboric acids (see p. 267). The iso-12-tungstosilicic acid is best prepared<sup>2</sup> by heating at 100° C. a solution containing sodium tungstate and sodium silicate, made slightly acid with sulphuric acid. On adding sulphuric acid and ether, oily drops separate and both isomeric forms of the acid are produced, the iso-acid being in the greater quantity. The acids may be separated by fractional crystallisation of their potassium salts, the 12-tungstosilicate crystallising first, and then the rhombic potassium iso-salt,  $K_4H_4[Si(W_2O_7)_6] \cdot 7H_2O$ . From this the acid may be obtained by Dreichsel's method. The acid yields triclinic crystals. If the potassium salt is heated with water in a sealed tube at 150° C. it is gradually transformed into its isomeride,  $K_4H_4[Si(W_2O_7)_6] \cdot 16H_2O$ .<sup>2</sup> The following salts are described by Marignac :



as well as the normal salts



The normal barium salt,  $Ba_4[Si(W_2O_7)_6] \cdot 27H_2O$ , is obtained<sup>3</sup> as a fine crystalline powder by adding barium chloride to a boiling solution of ammonium paratungstate saturated with silicic acid gel, and allowing the oil which separates to remain in contact with the mother liquor.

**10-Tungstosilicates.** When ammonia is added in large excess to a solution of 12-tungstosilicic acid, and the mixture boiled and continually shaken, an ammonium salt is formed, which crystallises in orthorhombic prisms and corresponds in composition to the formula  $(NH_4)_8[Si(W_2O_7)_5] \cdot 8H_2O$ .<sup>4</sup> The crystals are readily soluble in water, and on evaporation the solution yields an amorphous glass which is supposed to be the free acid. The same amorphous substance is obtained on shaking out with acid and ether according to Dreichsel's method. On neutralisation by means of bases, well-defined products are not obtained and the character of the amorphous glass appears doubtful. By the action of potassium carbonate on the tetrabasic potassium 12-tungstosilicate, a well-crystallised salt, of composition  $K_2[Si(OH)(W_2O_7)_5] \cdot 11H_2O$ , is obtained.<sup>5</sup> A corresponding guanidinium salt has also been prepared.

For complex silicovanadotungstates, see p. 258.

#### TUNGSTEN AND TITANIUM.

Complex tungstotitanates believed to correspond to the 12- and 10-tungsto-silicates have been described,<sup>6</sup> but their existence has not been confirmed.

<sup>1</sup> Marignac, *Ann. Chim. Phys.*, 1864, [4], 3, 48.

<sup>2</sup> Copaux, *Bull. Soc. chim.*, 1908, [4], 3, 191.

<sup>3</sup> Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1912, 77, 239; 1917, 101, 235.

<sup>4</sup> Copaux, *loc. cit.*; Rosenheim and Jänicke, *loc. cit.*; Marignac, *loc. cit.*

<sup>5</sup> Kehrman, *Zeitsch. anorg. Chem.*, 1904, 39, 98; Rosenheim and Jänicke, *loc. cit.*

<sup>6</sup> Lecarme, *Bull. Soc. chim.*, 1881, [2], 36, 17.

## TUNGSTEN AND ZIRCONIUM.

By dissolving zirconium hydroxide in solutions of ammonium and potassium paratungstates Hallopeau<sup>1</sup> claims to have prepared 10-tungstozirconates of composition  $4R_2O \cdot ZrO_2 \cdot 10WO_3 \cdot xH_2O$ . According to other investigators, however, zirconium hydroxide appears to be quite insoluble in paratungstate solutions.

## TUNGSTEN AND BORON.

**Tungsten Boride,  $WB_2$ ,** is produced when a mixture containing 4 grams of tungsten and 0.2 gram of boron is heated in an electric furnace,<sup>2</sup> or when an electric arc is passed between electrodes, made by pressing together finely powdered boron and tungsten, in a vacuum electric furnace.<sup>3</sup> The product is silvery and metallic on fracture, and consists of microscopic octahedral crystals. The boride is brittle, of hardness 8 and of density, according to Tucker and Moody, 9.6; Wedekind found the density at 20° C. to be 10.77. It is slowly attacked by concentrated acids, more readily by aqua regia. Chlorine decomposes it at 100° C. It readily dissolves in a fused mixture of sodium carbonate and potassium nitrate.

## TUNGSTOBORIC ACIDS AND TUNGSTOBORATES.

**12-Tungstoboric Acid,  $H_9[B(W_2O_7)_6] \cdot 28H_2O$ ,** is prepared<sup>4</sup> by the addition to 1 part of normal sodium tungstate and 1.5 parts of boric acid of sufficient water to form a clear solution on boiling. After a time a mixture of sodium borate and boric acid separates. This is filtered off, the mother-liquor is treated with more boric acid, a further precipitate is rejected, and the solution treated with sulphuric acid and ether according to Drechsel. The resulting oil is decomposed by cold water, and on evaporation in a vacuum, crystals of two isomeric acids separate simultaneously; those in larger quantity being transparent octahedra of 12-tungstoboric acid,  $H_9[B(W_2O_7)_6] \cdot 28H_2O$ ; those in smaller quantity, hexagonal bipyramidal crystals of *iso*-12-tungstoboric acid,  $H_9[B(W_2O_7)_6] \cdot 22H_2O$ .<sup>5</sup> The first acid is isomorphous with the 28-hydrates of the 12-tungsto- and 12-molybdo-phosphoric and silicic acids. It melts at 45° to 51° C. The addition of nitric acid to its concentrated solution precipitates a lower hydrate containing  $10H_2O$ . The hydrogen-ion concentration in a 0.05 N solution<sup>6</sup> is  $3.5 \times 10^{-3}$ .

A well-defined series of crystalline salts, of composition  $R_5H_4[B(W_2O_7)_6] \cdot xH_2O$  ( $R = NH_4, Li, K, Na, Ag$ ;  $R_2 = Ba, Ca, Cd, Cu$ ,

<sup>1</sup> Hallopeau, *Bull. Soc. chim.*, 1896, [3], 15, 917.

<sup>2</sup> Tucker and Moody, *Trans. Chem. Soc.*, 1902, 81, 14; Moissan, *Compt. rend.*, 1896, 123, 13; *Ann. Chim. Phys.*, 1896, [7], 8, 570.

<sup>3</sup> Wedekind, *Ber.*, 1913, 46, 1198.

<sup>4</sup> Copaux, *Compt. rend.*, 1908, 147, 973; *Ann. Chim. Phys.*, 1909, [8], 17, 217; *Zeitsch. anorg. Chem.*, 1911, 70, 297; *Bull. Soc. chim.*, 1913, [4], 13, 324. See also Klein, *Compt. rend.*, 1880, 91, 415, 474, 495, 1070; 1881, 93, 318, 492; *Bull. Soc. chim.*, 1880, [2], 33, 466; 34, 23; 1881, 35, 12; 36, 17; 1882, 37, 202; *Ann. Chim. Phys.*, 1883, [5], 28, 350; Mauro, *Bull. Soc. chim.*, 1880, [2], 33, 564; *Jahresber.*, 1880, 33, 351; *Gazzetta*, 1881, 11, 214; *Ber.*, 1881, 14, 1379.

<sup>5</sup> Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1911, 70, 423; 1912, 77, 239; 1917, 101, 235; Rosenheim and Schwer, *ibid.*, 1914, 89, 224.

<sup>6</sup> Brauer, *Dissertation*, Berlin, 1918.

Mg, Ni), has been obtained by careful addition of the metal hydroxide or carbonate to 12-tungstoboric acid. These salts are isomorphous with the corresponding salts of other 12-heteropolyacids; <sup>1</sup> for instance, in addition to the examples already given (see p. 265), the sodium salt,  $\text{Na}_5\text{H}_4[\text{B}(\text{W}_2\text{O}_7)_6]\cdot 27\text{H}_2\text{O}$ , is isomorphous with the similarly constituted sodium metatungstate,  $\text{Na}_6\text{H}_4[\text{H}_2(\text{W}_2\text{O}_7)_6]\cdot 27\text{H}_2\text{O}$ .<sup>2</sup> The equivalent conductivities of solutions of the sodium salt, containing  $\frac{1}{2}$  molecule in  $v$  litres at  $25^\circ \text{C}$ ., have been found <sup>2</sup> to be :

$v =$	32	64	128	256	512	1024
$\Lambda =$	183.9	196.0	203.2	213.6	225.3	235.3

These values correspond with those of a neutral pentabasic salt, but the neutralisation curve shows that at least two more of the hydrogen atoms are replaceable. A guanidinium salt,  $(\text{CN}_3\text{H}_6)_3\text{H}_3[\text{B}(\text{W}_2\text{O}_7)_6]$ , has been obtained, and, according to Copaux, the addition of mercurous nitrate to a solution of the sodium salt yields a crystalline precipitate of the normal mercurous salt,  $\text{Hg}_2[\text{B}(\text{W}_2\text{O}_7)_6]\cdot 12\text{H}_2\text{O}$ .

**Iso-12-tungstoboric Acid**,  $\text{H}_9[\text{B}(\text{W}_2\text{O}_7)_6]\cdot 22\text{H}_2\text{O}$ , prepared as above, has no definite melting-point, but decomposes on heating. According to Copaux, a potassium and a barium salt may be obtained by treating the acid with small quantities of the metallic hydroxide, but that these salts are distinct from the ordinary 12-tungstoborates has not yet been conclusively shown.

#### DETECTION AND ESTIMATION OF TUNGSTEN.

The analysis of materials containing tungsten is comparatively simple owing to the ease with which the metal can be converted into soluble alkali tungstates, and to the fact that the most stable oxide,  $\text{WO}_3$ , is almost insoluble in all mineral acids with the exception of hydrofluoric and phosphoric acids. The element is usually met with in its ores, chiefly wolframite and scheelite; in alloys, especially ferro-tungsten and tungsten steels; as the metal—tungsten powder, tungsten electric light filaments; as alkali tungstates and tungstic anhydride,  $\text{WO}_3$ .

**Detection.**—The finely powdered material is fused with excess of sodium carbonate or potassium hydrogen sulphate in a platinum crucible, or better, since there is serious loss of platinum in fusions of tungsten alloys,<sup>3</sup> with potassium hydroxide in a silver or nickel crucible. The cooled mass is extracted with boiling water and filtered. On acidifying with concentrated hydrochloric acid, and reducing by means of metallic tin,<sup>4</sup> a blue colour or precipitate indicates the presence of tungsten. If the reduction is continued for two days the colour becomes brown, due to the formation of tungsten dioxide. Other reducing agents, such as zinc, aluminium,<sup>5</sup> or stannous chloride,<sup>6</sup> may also be used, but the action of tin is most satisfactory and can easily be controlled.<sup>4</sup>

<sup>1</sup> Klein, *Ann. Chim. Phys.*, 1883, [5], 28, 392; Copaux, *Compt. rend.*, 1909, 148, 633; *Zeitsch. anorg. Chem.*, 1911, 70, 209.

<sup>2</sup> Rosenheim and Schwer, *Zeitsch. anorg. Chem.*, 1914, 89, 224.

<sup>3</sup> Seel, *Zeitsch. angew. Chem.*, 1922, 35, 643.

<sup>4</sup> Hartman, *Chem. News*, 1916, 114, 27, 45.

<sup>5</sup> Torossian, *Amer. J. Sci.*, 1914, [4], 38, 537.

<sup>6</sup> Mdivani, *Bull. Soc. chim.*, 1911, [4], 9, 122; *Bull. Soc. chim. Bely.*, 1911, 25, 41.

The only other metals likely to give a blue colour are columbium, vanadium, molybdenum, and titanium. The colour due to columbium disappears on dilution. The colour due to vanadium may be obtained by means of tartaric acid, which gives no colour with tungsten. The colour formed on reduction of molybdenum is from violet to black, while that due to titanium is violet; these elements can easily be separated from the tungsten before the reduction test is made.<sup>1</sup>

Solutions of alkali tungstates are precipitated by dilute mineral acids, yellow tungstic acid  $\text{H}_2\text{WO}_4$  or the white hydrate  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  being formed (see p. 205). The precipitate readily dissolves in alkalies, and on reduction yields the blue oxide.

A *microchemical* method for the identification of the tungstic acid precipitate consists in dissolving a portion in a few drops of concentrated ammonia and placing one drop on a slide; ammonium paratungstate soon crystallises as four-cornered plates on the edges of the drop, and as long needles in the centre.<sup>2</sup>

**Estimation.**—The most convenient form in which to weigh tungsten is the trioxide  $\text{WO}_3$ , which does not volatilise even at high temperatures. For the analysis of tungsten ores there are three methods of procedure in common use: <sup>3</sup> (1) A solution is obtained by digesting the finely powdered mineral with equal parts of hydrochloric and hydrofluoric acids. If tin is present it remains behind as stannic oxide. The solution is evaporated with excess of hydrochloric acid, and then boiled with a mixture of hydrochloric and nitric acids until all the hydrofluoric acid is expelled and the tungsten separates out as tungstic acid. This is dissolved on the filter by means of a little warm dilute ammonia, the solution being received in a weighed platinum dish. After evaporation on a water-bath the residue is ignited and weighed as  $\text{WO}_3$ . (2) The powdered ore is fused with alkali as already described (p. 268) and the mass extracted with boiling water. The solution contains alkali tungstate and any alkali silicate and stannate (if tin is present). After evaporation to dryness with excess of nitric acid, the residue is heated in an oven at  $120^\circ \text{C}$ . and then treated with a dilute solution of ammonium nitrate slightly acid with nitric acid. The residue is ignited in a platinum crucible with free access of air, when tungstic anhydride remains. The residue may contain silica, which can be removed by means of hydrofluoric acid, and a trace of stannic oxide, which may be volatilised as stannic chloride <sup>4</sup> by ignition with ammonium chloride. (3) The finely powdered mineral is heated, but not boiled, with aqua regia, the liquid evaporated to about one-third of its bulk and then diluted with water. After standing, the solution is decanted and the residue washed by decantation with hot water acidulated with hydrochloric acid. The residue is next treated with a solution of ammonia containing a little ammonium chloride until all the yellow tungstic acid is dissolved and a white residue of silica remains. The ammoniacal solution is evaporated to dryness in a platinum dish, the residue is

<sup>1</sup> See textbooks of analysis, e.g. Scott, *Standard Methods of Chemical Analysis*, 2nd ed. (New York, 1918), p. 448. Also for separation of W and Mo, see Marbauer, *J. Amer. Chem. Soc.*, 1915, 37, 86; Merrill, *ibid.*, 1921, 43, 2383; for separation of W and Ti, see Fenner, *Chem. Zeit.*, 1918, 42, 403.

<sup>2</sup> van Liempt, *Zeitsch. anorg. Chem.*, 1922, 122, 236. See also Vivario and Wagenaar, *Pharm. Weekblad*, 1917, 54, 157, who suggest the use of urotropine.

<sup>3</sup> Hartman, *loc. cit.*

<sup>4</sup> Dittler and von Graffenried, *Chem. Zeit.*, 1916, 40, 681.

gently heated to expel ammonium salts, and then strongly ignited. After cooling, it is moistened with hydrofluoric acid, evaporated to dryness and again ignited, and finally weighed as  $\text{WO}_3$ .

Many modifications of the above methods have been described.<sup>1</sup> If arsenic is present in the ore it may be removed<sup>2</sup> by treating the aqueous extract—after fusion with sodium carbonate and sodium peroxide—with phosphoric acid. This forms a complex with the tungsten, and the arsenic may be distilled off. It has been suggested that the formation of complex silicotungstates may be a source of error in the above methods of analysis.<sup>3</sup> Tungstates may conveniently be estimated by precipitating the mercurous salt (see p. 221) and converting it to the trioxide by ignition.<sup>4</sup> Use has been made of the fact that tungstic acid volatilises when heated in a current of carbon dioxide saturated with carbon tetrachloride vapour.<sup>5</sup> By collecting the product, evaporating with nitric acid and igniting, the pure anhydride is obtained. According to Gutbier and Weise,<sup>6</sup> tungstic acid in acetic acid solution is quantitatively separated by means of Busch's "nitron" acetate reagent. Organic precipitants have also been employed.<sup>7</sup>

Reliable **volumetric methods** for the estimation of tungstic acid are not known. An indirect method recently suggested for use with low-grade ores<sup>8</sup> consists in precipitating tungstic acid from a slightly acid solution by means of cinchonine hydrochloride, dissolving the precipitate in ammonium acetate solution, and adding an excess of a standard solution of lead acetate. After standing half an hour the excess of lead acetate is titrated with ammonium molybdate. Another volumetric process employs benzidine hydrochloride as precipitant.<sup>9</sup> The washed precipitate is mixed with water and titrated at 60° C. with decinormal sodium hydroxide, with phenolphthalein as indicator. It is necessary to boil at the end point in order to keep the solution free from carbon dioxide. The benzidine tungstate is readily hydrolysed, so that the result gives the total  $\text{WO}_3$  present.

**Colorimetric methods** of determination have been suggested.<sup>10</sup>

For the determination of the tungsten in commercial forms of the metal, gravimetric methods similar to the above are available.<sup>11</sup> The metal, when in the finely powdered condition, readily dissolves in a

<sup>1</sup> Marbaker, *J. Amer. Chem. Soc.*, 1915, 37, 86; Corti, *Anal. Soc. Quim. Argentina*, 1917, 5, 308; Travers, *Compt. rend.*, 1917, 165, 408.

<sup>2</sup> Dieckmann and Hilpert, *Ber.*, 1914, 47, 2444.

<sup>3</sup> Guglielmelli and Hordh, *Anal. Soc. Quim. Argentina*, 1917, 5, 81.

<sup>4</sup> For the analysis of complex tungstates containing arsenic, antimony, or vanadium, see Sweeney, *J. Amer. Chem. Soc.*, 1916, 38, 2377.

<sup>5</sup> Jannasch and Leiste, *J. prakt. Chem.*, 1918, [2], 97, 141.

<sup>6</sup> Gutbier and Weise, *Zeitsch. anal. Chem.*, 1914, 53, 426.

<sup>7</sup> von Knorre, *ibid.*, 1908, 47, 37; Tschilikin, *Ber.*, 1909, 42, 1302; Kafka, *Zeitsch. anal. Chem.*, 1913, 52, 601.

<sup>8</sup> Lavers, *Proc. Austral. Inst. Min. Met.*, 1921, p. 101. See *J. Soc. Chem. Ind.*, 1922, 41, 145a.

<sup>9</sup> Kantschew, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 729. Cf. von Knorre, *Ber.*, 1905, 38, 783; Arnold, *Zeitsch. anorg. Chem.*, 1914, 88, 74.

<sup>10</sup> Heath, *Chem. Trade J.*, 1920, 66, 629; Travers, *Compt. rend.*, 1918, 166, 416. For a colorimetric method of estimating small quantities of molybdenum in tungsten, see King, *Ind. Eng. Chem.*, 1923, 15, 350.

<sup>11</sup> Hodes, *Zeitsch. angew. Chem.*, 1917, 30, 240; Erlich, *Ann. Chim. anal.*, 1920, [2], 2, 102. For the estimation of P, As, S, C, and  $\text{SiO}_2$ , in metallic W, see Arnold, *Zeitsch. anorg. Chem.*, 1914, 88, 74, 333; for separation of Mo, see Koppel, *Chem. Zeit.*, 1924, 48, 801; Hall, *J. Amer. Chem. Soc.*, 1922, 44, 1462; for separation of Al, see Froboese and Froboese, *Zeitsch. anal. Chem.*, 1922, 61, 107.

mixture of ammonia and hydrogen peroxide, or in ammonium persulphate; <sup>1</sup> when massive, it is best dissolved electrolytically, using ammonia containing a little ammonium persulphate in a platinum dish as cathode, but small pieces will also dissolve readily in fused alkali nitrate.

Lottermoser has described <sup>2</sup> two methods for estimating the amount of colloidal tungsten in commercial tungsten powders. In the first method the powder is shaken with water and the mixture allowed to sediment for two days. The supernatant liquid is removed and replaced by water, and the shaking and sedimentation repeated as long as there is any measurable quantity of tungsten in the liquid. The sediment, when dried and weighed, gives the non-colloidal portion. The second method consists in examining the solutions from which the powder has sedimented. The quantity of colloidal tungsten present is estimated by means of its absorption of light from a quartz mercury lamp, which passes through the solution on to a potassium photoelectric cell. <sup>3</sup> The absorption is measured by deflection of a galvanometer.

In the analysis of tungsten steels the sample may be dissolved in hydrochloric acid or dilute sulphuric acid in absence of air. The tungsten remains undissolved and is ignited, fused with sodium carbonate, and estimated by ordinary methods. <sup>4</sup>

Ferrotungsten alloys decompose completely when fused with ammonium sulphate and concentrated sulphuric acid. <sup>5</sup> If the mass is extracted with water the iron may be separated from the solution by means of ammonia; the tungstic acid remains in the residue, and any going into solution may be recovered by addition of hydrochloric acid. A method of analysis which appears suitable for rapid industrial control of the proportion of tungsten in iron alloys and tool steels <sup>6</sup> employs a 50 per cent. solution of nitric acid, containing a little hydrofluoric acid in order to dissolve the sample. Subsequent digesting with concentrated sulphuric acid eliminates hydrofluoric acid and causes complete precipitation of tungstic acid, which may be ignited and weighed in the usual way.

Reliable **electrolytic methods** for the analysis of tungsten compounds are not known.

<sup>1</sup> Arnold, *loc. cit.*

<sup>2</sup> Lottermoser, *Kolloid Zeitsch.*, 1922, 30, 53.

<sup>3</sup> See also van Liempt, *Rec. Trav. chim.*, 1924, 43, 30.

<sup>4</sup> Arnold, *loc. cit.*; van Duin, *Chem. Weekblad*, 1917, 14, 169.

<sup>5</sup> Löwy, *Zeitsch. angew. Chem.*, 1919, 32, 379.

<sup>6</sup> Losana and Carozzi, *Giorn. Chim. Ind. Appl.*, 1922, 4, 299. See also Fieber, *Chem. Zeit.*, 1912, 36, 334; Dittler and von Gräffenried, *ibid.*, 1916, 40, 681.

## CHAPTER VIII.

### URANIUM.

Symbol, U. Atomic weight, 238·17.

**Occurrence.**—Uranium is not widely distributed in nature. It occurs as an essential constituent in only a few minerals, and these are not very abundant. The most important ore is *pitchblende*<sup>1</sup> or *uraninite*, which may contain 40 to 90 per cent. of uranium oxide, usually expressed as  $U_3O_8$ , together with small quantities of iron, lead, bismuth, thorium, and the rare earths. It occurs massive with indistinct crystallisation, and also in grains; crystals are rare, but well-defined octahedra and cubes are sometimes found. The mineral occurs as a constituent of granitic rocks, and also in metalliferous veins with sulphides of silver, lead, iron, cobalt, nickel, and copper. It is brittle, of hardness 5·5 and, when crystalline, of density 9·0 to 9·7; of massive altered forms, the density varies from 6·4 upwards. In appearance uraninite resembles pitch and is usually black and slightly lustrous, but some specimens are grey to greenish or brownish. It is found at Joachimsthal in Bohemia,<sup>2</sup> at various localities in Saxony, Hungary, Norway, and Turkey; in Connecticut, North Carolina, Colorado, and Utah; in Bengal<sup>3</sup> and East Africa; associated with monazite in the Villeneuve mica veins, Quebec; and associated with torbernite (see below) near Redruth in Cornwall.<sup>4</sup> In composition the mineral appears to be essentially a uranate of uranyl, but the ratio  $UO_2 : UO_3$  varies widely, even in specimens from the same locality, and it has been suggested<sup>5</sup> that the mineral was originally the dioxide,  $UO_2$ , isomorphous with thorianite,  $ThO_2$ , and that the trioxide has been produced by oxidation. The formula  $(UO_2)_3(UO_3)_2$ , or  $U^{IV}_3(U^{VI}O_6)_2$ , has been proposed for the purified mineral,<sup>6</sup> but it is not of general application.<sup>7</sup>

*Cleveite*<sup>8</sup> and *bröggerite*<sup>9</sup> are varieties of uraninite, rich in thorium and rare earths, occurring in Norway. Cleveite is generally found in

<sup>1</sup> Klaproth, *Beiträge*, 1789, 2, 197; *Crell's Annalen*, 1789, 2, 387; Ebelmen, *Ann. Chim. Phys.*, 1843, [3], 8, 498; Hermann, *J. prakt. Chem.*, 1859, 76, 326; Zimmermann, *Annalen*, 1886, 232, 300; Szilárd, *Compt. rend.*, 1907, 145, 463.

<sup>2</sup> Janda, *Chem. Zentr.*, 1902, ii., 150.

<sup>3</sup> Tipper, *Rec. Geol. Surv. India*, 1919, 50, 255.

<sup>4</sup> See also Laby, *J. Roy. Soc. N.S.W.*, 1909, 43, 28; Tschernik, *Bull. Acad. Sci. Petrograd*, 1909, [6], 3, 1203.

<sup>5</sup> Schoep, *Bull. Soc. chim. Belg.*, 1923, 32, 274.

<sup>6</sup> Blomstrand, *J. prakt. Chem.*, 1884, [2], 29, 191; Schoep, *loc. cit.*

<sup>7</sup> Hillebrand, *Amer. J. Sci.*, 1890, 40, 384; 1891, 42, 390; *Bull. U.S. Geol. Survey*, 1889, No. 78.

<sup>8</sup> Nordenskjöld, *Geol. För. Förh. Stockholm*, 1878, 4, 28.

<sup>9</sup> Blomstrand, *ibid.*, 1884, 7, 60.

cubic crystals of density 7.49, whilst bröggerite yields octahedra of density 9.03. *Nivenite* is similar to cleveite, and like the latter mineral contains about 10 per cent. of the yttrium earths. It occurs in Texas, and is generally found massive with indistinct crystallisation. Hardness 5.5; density 8.01. It dissolves more readily than other varieties of uraninite in dilute acid, being completely decomposed by digesting with very dilute sulphuric acid at 100° C. A very pure form of uraninite occurs <sup>1</sup> in the Morogoro district of Tanganyika Territory, in the form of crystals containing 87 to 88 per cent.  $\text{U}_3\text{O}_8$ . These are largely altered to a yellow uranyl carbonate known as *rutherfordine*.

*Uranothallite* <sup>2</sup> occurs as an incrustation, consisting of minute indistinct crystals, on uraninite at Joachimsthal. It contains the carbonates of calcium and uranium, its composition corresponding to the formula  $2\text{CaCO}_3 \cdot \text{U}(\text{CO}_3)_2 \cdot 10\text{H}_2\text{O}$ . It is greenish, translucent, and vitreous in appearance; hardness 2.5 to 3.0. *Liebigite* <sup>3</sup> is a similar mineral, found near Adrianople, Turkey, and at Joachimsthal, the composition of which is probably  $\text{CaCO}_3 \cdot (\text{UO}_2)\text{CO}_3 \cdot 20\text{H}_2\text{O}$ . It is transparent, of a beautiful apple-green colour, and has hardness 2.5. *Voglite*, also found at Joachimsthal in aggregations of green crystalline scales, contains carbonates of calcium, uranium, and copper.<sup>4</sup>

*Gummite* is an alteration-product of uraninite of doubtful composition. It appears to be a hydrated silicate of uranium, containing lead, calcium, and sometimes iron. It occurs in rounded or flattened pieces, reddish yellow to reddish brown in colour, resembling gum. Hardness 2.5 to 3.0; density 3.9 to 4.2. It is found in North Carolina and in Saxony. Varieties of gummite found near Joachimsthal are known as *eliasite* and *pittinite*; *soddite* and *chinkolobwite* <sup>5</sup> from Katanga, Belgian Congo, contain uranium and silica, and probably have the composition  $12\text{UO}_3 \cdot 5\text{SiO}_2 \cdot 14\text{H}_2\text{O}$ ; *yttrogummite* <sup>6</sup> occurs with cleveite; *thorogummite* <sup>7</sup> is found in Texas. A uraninite partly altered to gummite, and known as *coracite*, occurs north of Lake Superior.<sup>8</sup>

*Uranophane* <sup>9</sup> or *uranotil*, <sup>10</sup> a further alteration-product of uraninite, is a hydrated silicate of uranium and calcium, of composition <sup>11</sup>  $\text{CaO} \cdot 2\text{UO}_3 \cdot 3\text{SiO}_2 \cdot 7\text{H}_2\text{O}$ . It is found with the uranium minerals in Silesia, Bavaria, Saxony, and North Carolina, occurring in aggregations of minute yellow acicular prisms, often as an incrustation upon, and penetrating into, gummite.

*Uranospharite*, a bismuth uranate of composition <sup>12</sup>  $\text{Bi}_2\text{O}_3 \cdot 2\text{UO}_3 \cdot 3\text{H}_2\text{O}$ , occurs in Saxony in orange-yellow half-globular aggregated forms, of hardness 2.3 and density 6.36.

*Autunite*, *calco-uranite*, or *lime-uranite*, <sup>13</sup> a hydrated phosphate of

<sup>1</sup> Marekwald, *Centr. Min.*, 1906, p. 761; *Landw. Jahrb.*, 1909, 38, v., 423.

<sup>2</sup> Schrauf, *Zeitsch. Kryst. Min.*, 1882, 6, 410.

<sup>3</sup> Smith, *Amer. J. Sci.*, 1848, [2], 5, 336; 1851, [2], 11, 259.

<sup>4</sup> See also Antipoff, *Zeitsch. Kryst. Min.*, 1902, 36, 175.

<sup>5</sup> Schoep, *Bull. Soc. Belg. Geol.*, 1923, 33, 87; *Bull. de Belg.*, 1923, 32, 345; *Compt. rend.*, 1922, 174, 1066; 1921, 173, 1186.

<sup>6</sup> Nordenskjöld, *loc. cit.*

<sup>7</sup> Hidden and Mackintosh, *Amer. J. Sci.*, 1889, [3], 38, 480.

<sup>8</sup> Whitney, *ibid.*, 1849, [2], 7, 433; Genth, *ibid.*, 1857, [2], 23, 421.

<sup>9</sup> Websky, *Zeitsch. Geol. Ges.*, 1853, 5, 427; 1859, 11, 384.

<sup>10</sup> Boricky, *Ber. Böhm. Ges.*, 1870, p. 36.

<sup>11</sup> Watson, *Amer. J. Sci.*, 1902, [4], 13, 464; Genth, *Amer. Chem. J.*, 1879, 1, 83.

<sup>12</sup> Winkler, *J. prakt. Chem.*, 1873, [2], 7, 5.

<sup>13</sup> Berzelius, *Jahresber.*, 1823, 4, 46.



uranium and calcium,<sup>1</sup>  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , is generally found with uraninite. One of its chief sources is near Autun in France, but it also occurs in various localities in Germany and the United States, in Madagascar, Portugal,<sup>2</sup> near Limoges, and in Cornwall. It usually occurs as thin, yellow, transparent or translucent, tabular crystals of the orthorhombic system, or in foliated aggregates with micaceous structure, with hardness 2 to 2.5 and density 3.05 to 3.19. Its uranium content is equivalent to 55 to 62 per cent.  $\text{UO}_3$ . The Cornish autunite appears to be distinct from the original mineral from Autun,<sup>3</sup> and to belong to two different species which have been named *bassetite* and *uranospathite*. Both form yellow crystals with a micaceous cleavage; bassetite is monoclinic,

$$a : b : c = 0.3473 : 1 : 0.3456 ; \beta = 89^\circ 17',$$

and of density 3.1; uranospathite is orthorhombic and pseudotetragonal, and of density 2.5.<sup>4</sup>

*Torbernite*,<sup>5</sup> *torberite*, *chalcolite*, *cupro-uranite*, or *uranium mica* is a related mineral to autunite, but is greenish in colour and yields tetragonal crystals of density 3.4 to 3.6 and of hardness 2.0 to 2.5. It is a hydrated phosphate of uranium and copper,  $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,<sup>6</sup> but the phosphorus may in part be replaced by arsenic. The mineral exhibits a perfect basal cleavage which often imparts to it a micaceous structure. It occurs chiefly in Cornwall<sup>7</sup> and in the pitchblende districts of Saxony, Bohemia, and Belgium. It generally contains 56 to 60 per cent.  $\text{UO}_3$ . Both torbernite and autunite are included under the common name of uranite. Minerals closely related to these are: *zeunerite*, a greenish arsenate of copper and uranium,  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ;<sup>8</sup> *uranospinite*, an arsenate corresponding to autunite, of composition  $\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ;<sup>9</sup> *uranocircite*, a phosphate of barium and uranium,  $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ;<sup>9</sup> *walpurkite*, probably a basic arsenate of bismuth and uranium;<sup>10</sup> *dewindtite* and *stasite*, apparently dimorphous forms of a lead uranium phosphate, of composition  $4\text{PbO} \cdot 8\text{UO}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ ,<sup>11</sup> which occur with torbernite in the Katanga district, Belgian Congo.

*Phosphuranylite*,<sup>12</sup> a hydrated phosphate,  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ , occurs as a lemon-yellow pulverulent incrustation on quartz, felspar, and mica in North Carolina.

*Trögerite* is a hydrated arsenate, of composition<sup>10</sup>  $(\text{UO}_2)_3(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}$ , found in Saxony and Portugal.<sup>13</sup>

<sup>1</sup> Winkler, *J. prakt. Chem.*, 1873, [2], 7, 5; Church, *J. Chem. Soc.*, 1875, 28, 109; Jannettaz, *Bull. Soc. min. de France*, 1887, 10, 17.

<sup>2</sup> Pereira-Forjaz, *Compt. rend.*, 1917, 164, 102; Strutt, *Proc. Roy. Soc.*, 1909, A, 83, 70.

<sup>3</sup> Hallimond, *Min. Mag.*, 1915, 17, 221.

<sup>4</sup> For spectroscopic examination of autunite and torbernite, see Gray, *Phil. Mag.*, 1909, [6], 18, 816.

<sup>5</sup> Dana, *Amer. J. Sci.*, 1867, [2], 44, 147.

<sup>6</sup> Werther, *J. prakt. Chem.*, 1848, 43, 334; Pisani, *Compt. rend.*, 1861, 52, 817; Church, *Chem. News*, 1865, 12, 183; Winkler, *J. prakt. Chem.*, 1873, 7, 10.

<sup>7</sup> Rudler, *Handbook to British Minerals*, H.M.S.O., 1905, p. 81.

<sup>8</sup> Winkler, *J. prakt. Chem.*, 1873, 7, 8; Pereira-Forjaz, *loc. cit.*

<sup>9</sup> Winkler, *loc. cit.*; Church, *Min. Mag.*, 1877, 1, 236.

<sup>10</sup> Winkler, *loc. cit.*

<sup>11</sup> Schoep, *Compt. rend.*, 1922, 174, 623, 875.

<sup>12</sup> Genth, *Amer. Chem. J.*, 1879, 1, 92.

<sup>13</sup> Pereira-Forjaz, *Compt. rend.*, 1917, 164, 102.

*Carnotite*<sup>1</sup> is a double vanadate of potassium and uranium, of probable composition  $K_2(VO_2)_2(VO_4)_2 \cdot 8H_2O$ ,<sup>2</sup> but generally very impure with silica. It occurs as a yellow crystalline powder, or in loosely cohering masses, chiefly in Colorado and Utah, but also in South Australia<sup>3</sup> and Portugal.<sup>4</sup> The mineral has attained considerable importance in America as a source of uranium and radium.

Other minerals containing uranium are: *thorianite*, generally regarded as an isomorphous mixture of the dioxides of uranium and thorium, containing 10 to 30 per cent.  $UO_2$ , found chiefly in Ceylon;<sup>5</sup> *uranothorite*, a name given to varieties of thorite containing uranium, as much as 10 per cent.  $UO_3$ , sometimes being present; *gilpinite*, occurring in Colorado in aggregates of minute yellow crystals intermixed with gypsum on pitchblende and copper ore, and having the composition  $RO \cdot UO_3 \cdot SO_3 \cdot 4H_2O$  ( $R = Cu, Fe, Na_2$ );<sup>6</sup> *uranopilite*, from Cornwall, is a similar mineral to gilpinite and probably identical with it;<sup>6</sup> *euxenite* and *polycrase*,<sup>7</sup> columbates and titanates of yttrium, erbium, cerium, and uranium, containing 4 to 16 per cent. uranium; *priorite* and *blomstrandine-priorite*, similar to euxenite and polycrase, but containing less uranium;<sup>8</sup> *blomstrandite*,<sup>9</sup> containing tantalum in addition to columbium and titanium; *tyrite*,<sup>10</sup> complex columbates of yttrium, cerium, uranium, calcium, and iron; *pyrochlore*, columbate of calcium rich in uranium;<sup>10</sup> *samarskite*, a uranotantalate of iron and yttrium, found in Siberia and North Carolina;<sup>11</sup> *fergusonite*, complex columbates of yttrium, cerium, uranium, calcium, and iron;<sup>12</sup> *brannerite*<sup>13</sup> from Idaho and *delorenzite*<sup>14</sup> from Piedmont are probably complex titanates. Many other rare earth minerals, such as *æschénite*,<sup>15</sup> *cérite*,<sup>16</sup> *xénotime*,<sup>17</sup> *monazite*,<sup>18</sup> and *ytthrocrastite*,<sup>19</sup> contain small quantities of uranium.<sup>20</sup> Traces also occur

<sup>1</sup> Friedel and Cumenge, *Compt. rend.*, 1899, 128, 532; *Bull. Soc. min.*, 1899, 22, 26; Hillebrand and Ransome, *Amer. Chem. J.*, 1900, [4], 10, 138; Boltwood, *Amer. J. Sci.*, 1904, 18, 97; Adams, *ibid.*, 1905, 19, 321; Crook and Blake, *Min. Mag.*, 1910, 15, 171; Moore and Kithil, "A Preliminary Report on Uranium, Vanadium, and Radium," Washington, 1913, *Bureau of Mines Dept. of the Int. Bull.*, 70.

<sup>2</sup> See this series, Vol. III., Part I., p. 266, footnote.

<sup>3</sup> Ward, *Mining Journal*, 1913, 103, 1134.

<sup>4</sup> Percin-Forjaz, *loc. cit.*

<sup>5</sup> Troost and Ouvrard, *Compt. rend.*, 1882, 102, 1422; Hillebrand, *Zeitsch. anorg. Chem.*, 1893, 3, 243; *Bull. U.S. Geol. Surv. Nr.*, 1893, p. 113; Dunstan, *Nature*, 1904, 59, 510, 533, 559; Coomaraswamy, *Mineralogical Survey of Ceylon*, 1904; Dunstan and Jones, *Proc. Roy. Soc.*, 1906, 77, A, 546; Büchner, *ibid.*, 1906, 78, A, 385; Szilárd, *Compt. rend.*, 1907, 145, 463; Kobayashi, *Sci. Rep. Tôhoku Imp. Univ. Sendai Japan*, 1912, i., 201.

<sup>6</sup> Larsen and Brown, *Amer. Min.*, 1917, 2, 75.

<sup>7</sup> Scheerer, *Pogg. Annalen*, 1840, 50, 149; 1844, 62, 430; 1847, 72, 566.

<sup>8</sup> Brögger, *Die Mineralien der Südnorwegischen Granitpegmutilgänge*, 1906, p. 98.

<sup>9</sup> Lindström, *Geologiska Föreningens i Stockholm Förhandlingar*, 1874, 2, 162; Lacroix, *Compt. rend.*, 1912, 154, 1040.

<sup>10</sup> Rammelsberg, *Pogg. Annalen*, 1871, 144, 191; 1873, 150, 198.

<sup>11</sup> Rammelsberg, *ibid.*, 1877, 160, 658.

<sup>12</sup> Rammelsberg, *ibid.*, 1873, 150, 200.

<sup>13</sup> Hess and Wells, *J. Franklin Inst.*, 1920, 189, 225.

<sup>14</sup> Zambonini, *Zeitsch. Kryst. Min.*, 1908, 45, 76.

<sup>15</sup> Marignac, *Ann. Chim. Phys.*, 1868, [4], 13, 24.

<sup>16</sup> Rammelsberg, *Pogg. Annalen*, 1859, 107, 631.

<sup>17</sup> Krauss and Reitingen, *Zeitsch. Kryst. Min.*, 1901, 34, 268.

<sup>18</sup> Hofmann and Zerban, *Chem. News*, 1902, 85, 100; Metzger, *J. Amer. Chem. Soc.*, 1902, 24, 901.

<sup>19</sup> Hidden and Warren, *Amer. J. Sci.*, 1906, [4], 22, 515.

<sup>20</sup> For table of principal U and Th minerals, see Szilárd, *Le Radium*, 1909, 6, 233.

in *kolm*, a variety of bituminous coal found in Sweden, the ash of which contains 1 to 3 per cent.  $U_3O_8$ .

The presence of uranium in the sun has been shown spectroscopically.<sup>1</sup>

**History.**—Previous to 1789 the mineral pitchblende had been considered to be an ore of zinc or of iron, but in that year Klaproth<sup>2</sup> suggested that it contained a new element, to which he gave the name uranium, in honour of Herschel's discovery of the planet Uranus in 1781. By reduction of the mineral at a high temperature, a product was obtained<sup>3</sup> which was believed to be the metal, but which was later recognised as the oxide  $UO_2$ . The formation of uranyl salts (see p. 287), in which this oxide plays a part analogous to that of a metallic element, supported the view that the metal had been isolated, but in 1840 Péligot prepared a new chloride, uranous chloride (see p. 294), whose composition was not in agreement with the idea that the so-called "uranium" was an element, and in 1842 he prepared the true metal by reducing his chloride with potassium.<sup>4</sup> He also showed that the substance hitherto regarded as the element was in reality an oxide (see p. 300).<sup>5</sup>

The nature of uranium minerals was later investigated by Hillebrand,<sup>6</sup> and in 1889 a gas, assumed to be nitrogen, was obtained from pitchblende by treating it with dilute sulphuric acid. The presence of this gas was remarkable, since nitrogen was not known to be present in any other mineral belonging to the original crust of the earth. After the discovery of argon,<sup>7</sup> however, the gas was re-examined by Ramsay,<sup>8</sup> who observed that it gave a spectrum identical with that observed in the sun's chromosphere by Lockyer in 1868, and attributed to the presence of an unknown element named helium. Thus terrestrial helium was discovered. It was first obtained from the mineral cleveite; Cornish pitchblende yields only a small quantity of the gas. The production of helium from uranium preparations has also been observed.<sup>9</sup>

The radioactivity of uranium was discovered in 1896 by Becquerel.<sup>10</sup> Two years later, Madame Curie,<sup>11</sup> observing that the radioactivity of pitchblende was greater than that of the element uranium, suggested that small quantities of a more active element were probably present in the mineral. This supposition led to the extraction of a chloride of the new element and to the subsequent discovery of radium.<sup>12</sup> The

<sup>1</sup> Lockyer, *Phil. Mag.*, 1879, 6, 161.

<sup>2</sup> Klaproth, *Crell's Annalen*, 1789, 2, 400; *Beiträge*, 1789, 2, 387.

<sup>3</sup> Klaproth, *loc. cit.*; Arfvedson, *Pogg. Annalen*, 1824, 1, 245; *Schweigger's J.*, 1825, 44, 8. See also Berzelius, *Pogg. Annalen*, 1824, 1, 359; *Schweigger's J.*, 1825, 44, 191; *Jahresber.*, 1843, 22, 116.

<sup>4</sup> Péligot, *Compt. rend.*, 1841, 12, 735; 1846, 22, 487; 1856, 42, 73; *Ann. Chim. Phys.*, 1842, [3], 5, 5.

<sup>5</sup> Péligot's work was confirmed by Rammelsberg, *Pogg. Annalen*, 1842, 55, 318; 56, 125; Ebelmen, *Ann. Chim. Phys.*, 1842, [3], 5, 189; Wertheim, *ibid.*, 1844, [3], 11, 49; *J. prakt. Chem.*, 1843, 29, 209.

<sup>6</sup> Hillebrand, *Bull. U.S. Geol. Survey*, 1889, No. 78; *Amer. J. Sci.*, 1890, 40, 384; 1891, 42, 390.

<sup>7</sup> See this series, Vol. I., Part II.  
<sup>8</sup> Ramsay, *Proc. Roy. Soc.*, 1895, 58, 65, 81; 59, 325. See also Lockyer, *ibid.*, 58, 67; also pp. 113, 116, 192, 193; 59, 342.

<sup>9</sup> Soddy, *Nature*, 1908, 79, 129; *Le Radium*, 1908, 5, 361; *Physikal. Zeitsch.*, 1909, 10, 41.

<sup>10</sup> Becquerel, *Compt. rend.*, 122, 420.

<sup>11</sup> Curie, *ibid.*, 1898, 126, 1101.  
<sup>12</sup> See this series, Vol. III., Part I. For Radioactivity of Uranium see this Vol., Chap. X.

remarkable properties of this extraordinary element has caused the mining of uranium minerals to attain very considerable importance, and owing to the fact that even from the purest uranium earths not more than about 3·4 parts of radium to ten million parts of uranium can be obtained, the output at present is insufficient to meet the demand.

**Treatment of Uranium Minerals.**—The chief source of uranium compounds is uraninite, but at the present time the working up of all uranium minerals has for its main object the extraction of radium,<sup>1</sup> and the uranium salts are merely produced as by-products. The methods in use vary according to the nature of the desired product, which may be ammonium or sodium diuranate, or uranyl nitrate.

The mechanically dressed ore is first roasted in order to remove sulphur, arsenic, and other volatile ingredients, and then heated in a reverberatory furnace with sodium carbonate or sodium sulphate. The product is extracted with warm dilute sulphuric acid, whereupon the uranium passes into solution, whilst the radium remains in the residue with calcium, barium, and lead. This residue, which is the starting material for the extraction of radium, also contains silica and small quantities of copper, bismuth, arsenic, antimony, iron, aluminium, manganese, zinc, nickel, cobalt, thallium, vanadium, columbium, tantalum, and rare earths.

The acid filtrate is treated with an excess of sodium carbonate solution, whereby basic carbonates of iron, aluminium, nickel, and cobalt are precipitated, while the uranium remains in solution as sodium uranyl carbonate.<sup>2</sup> The solution is neutralised by adding sulphuric acid and boiling, and on evaporation, sodium diuranate,  $\text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ , separates as a heavy yellow precipitate. If ammonium carbonate is used instead of sodium carbonate, or if the solution of sodium uranyl carbonate is boiled with ammonium sulphate, ammonium diuranate is obtained.<sup>3</sup> In order to obtain uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , the ammonium diuranate may be heated and the residue dissolved in nitric acid; or the original ore after roasting may be dissolved in nitric acid and the solution evaporated to dryness, the residue then being digested with water, filtered, and allowed to crystallise.<sup>4</sup> The uranyl nitrate is purified by recrystallisation from water.<sup>5</sup>

Carnotite may be fused with potassium hydrogen sulphate and the residue extracted with water. From the solution the double sulphates of potassium with uranium and vanadium may be obtained by crystallisation. These are reduced by means of zinc and sulphuric acid, and the vanadium precipitated from the solution by means of ammonia and ammonium carbonate. Ammonium diuranate separates from the filtrate on boiling.<sup>6</sup>

<sup>1</sup> See this series, Vol. III., Part I., p. 268.

<sup>2</sup> Patern, *Dingl. poly. J.*, 1854, **132**, 36; 1856, **141**, 371; *J. prakt. Chem.*, 1849, [1], **46**, 182; 1850, **51**, 122; 1854, **61**, 379; 1856, **69**, 118.

<sup>3</sup> See Giesecke, *Dingl. poly. J.*, 1852, **124**, 355; *J. prakt. Chem.*, 1852, **55**, 445; Wöhler, *Pogg. Annalen*, 1845, **64**, 94.

<sup>4</sup> Péligot, *Ann. Chim. Phys.*, 1844, [3], **12**, 557; Ebelmen, *ibid.*, 1842, [3], **5**, 186.

<sup>5</sup> Wilke-Dörfurt, *Wiss. Veröffentl. Siemens-Konzern*, 1920, **1**, 143; *Chem. Zentr.*, 1921, **i.**, 170.

<sup>6</sup> Gin, *Chem. Zentr.*, 1906, **ii.**, 1172. See also Ohly, *Chem. Zentr.*, 1906, **ii.**, 465; Haynes, *Mines and Minerals*, 1909, **30**, No. 3, 139; Moore and Kithil, "A Preliminary Report on Uranium, Vanadium, and Radium," Washington, 1913, *Bureau of Mines Dept. of the Int. Bull.*, 70.

**Preparation of Uranium.**—The isolation of the metal in a state of purity is accomplished only with difficulty. Three methods of procedure have been suggested, namely, (1) by reduction of urano-uranic oxide, (2) by reduction of uranous chloride, and (3) by electrolysis. The best results have been obtained by the first method, which also possesses an advantage in using as the starting material an oxide which is a commercial product.

1. *Reduction of Urano-uranic Oxide,  $U_3O_8$ .* This was first accomplished by Moissan,<sup>1</sup> who heated 500 parts of the oxide with 40 parts of sugar carbon<sup>2</sup> in an arc furnace. Complete reduction only takes place above  $1500^{\circ}C$ .<sup>3</sup> On a commercial scale, uranium of 96 to 98 per cent. purity can be obtained. The product always contains carbon. The oxide may also be reduced by heating with magnesium or

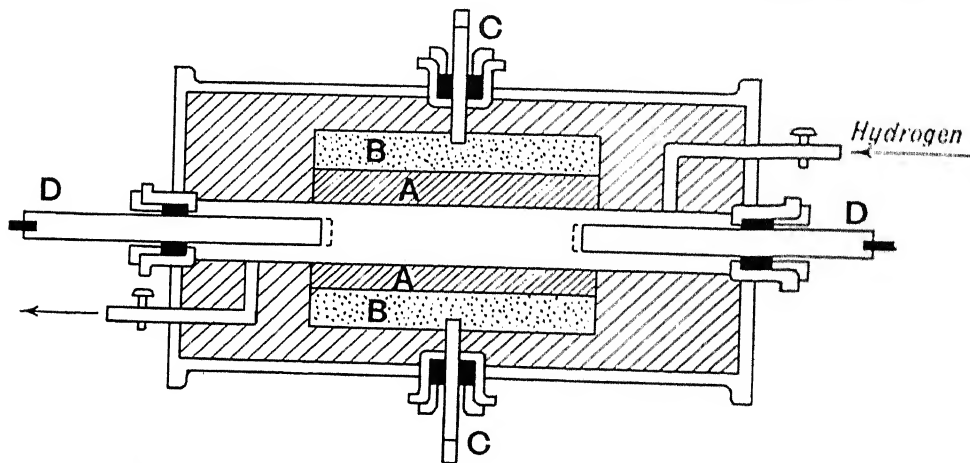


Fig. 5.—Type of furnace used by Rideal for the preparation of uranium.

AA, Magnesia tube.

BB, Carbon resistance.

CC, DD, Electrodes.

aluminium powder.<sup>4</sup> Rideal<sup>5</sup> obtained uranium of 98 to 99 per cent. purity by heating, in a tube of pure magnesia, a mixture containing 80 per cent. of the oxide and 20 per cent. of magnesium powder which had been pressed into rods by means of an oil press. The tube was heated in an apparatus (fig. 5) which was a combination of resistance and arc furnace. The apparatus was first filled with hydrogen, and when the temperature had been raised sufficiently by resistance heating, the rods became conducting, and an arc was passed through the tube from a second pair of electrodes connected with 110-volt mains, whereupon the magnesium vapour reduced the uranium oxide to the metal. The finely divided "uranium black" produced was in a pyrophoric

<sup>1</sup> Moissan, *Compt. rend.*, 1896, 122, 1088.

<sup>2</sup> See also Aloy, *Bull. Soc. chim.*, 1901, [3], 25, 344.

<sup>3</sup> Greenwood, *Trans. Chem. Soc.*, 1908, 93, 1492.

<sup>4</sup> Moissan, *Compt. rend.*, 1896, 122, 1302; Stavenhagen, *Ber.*, 1899, 32, 3065; Stavenhagen and Schuchard, *ibid.*, 1902, 35, 909; Aloy, *Bull. Soc. chim.*, 1901, [3], 25, 153; Giolitti and Tavanti, *Gazzetta*, 1908, 38, ii., 239.

<sup>5</sup> Rideal, *J. Soc. Chem. Ind.*, 1914, 33, 673.

condition, so that it could not be immediately exposed to the air; the hydrogen was therefore first displaced by carbon dioxide. Excess of magnesium was removed by washing with dilute acetic acid. By heating urano-uranic oxide with sodium and magnesium, in presence of calcium chloride, in a steel cylinder, to bright red heat, Rideal<sup>1</sup> obtained a greyish-black powder containing 99.4 to 99.6 per cent. uranium with traces of iron.

2. *Reduction of Uranous Chloride.*—The metal was first produced by Péligré<sup>2</sup> by the action of potassium on uranous chloride, and Zimmermann<sup>3</sup> obtained the metal as a black powder by reducing with sodium in presence of sodium chloride. Rideal,<sup>4</sup> repeating Zimmermann's experiments, and heating at 800° C. in a resistance furnace for forty-five minutes, obtained, after washing with alcohol and water, a brown powder containing 99.3 per cent. uranium. According to Moissan<sup>5</sup> the product is liable to be impure to a varying degree with iron (up to 2 per cent.) and sodium chloride; he therefore used the double chloride,  $\text{UCl}_4 \cdot 2\text{NaCl}$ , which is less hygroscopic than uranous chloride, and obtained a product which he considered was 99.4 per cent. uranium. Moore also obtained an exceedingly pure product<sup>6</sup> by reducing carefully purified uranous chloride with pure sodium by heating *in vacuo* in a steel bomb, and extracting the metal in an atmosphere of dry nitrogen. Substitution of magnesium for sodium, and of uranous fluoride for uranous chloride, have been suggested, but the results are not satisfactory.

3. *Electrolytic Methods.*—Moissan<sup>7</sup> obtained the metal by electrolysis of the double sodium uranium chloride in an atmosphere of hydrogen, using carbon electrodes. Férée,<sup>8</sup> by electrolysis of an aqueous solution of uranous chloride, using a mercury cathode, obtained a uranium amalgam, from which he isolated the uranium by distilling off the mercury *in vacuo*. However, uranium cannot be obtained in any quantity by this means.

**Physical Properties.**—Pure uranium is a lustrous white metal. When prepared by electrolysis of uranous chloride it is deposited as small glistening crystals;<sup>7</sup> by reduction of the oxide it is usually obtained as a brown or black powder. The metal is malleable, but less so than thorium;<sup>9</sup> it is very ductile and is capable of taking a high polish. It is not hard enough to scratch glass. Its density at 13° C. is 18.685.<sup>10</sup> The metal, when free from iron, is slightly paramagnetic, the susceptibility being  $11 + 0.9 \times 10^{-6}$ .

The position of the metal in the electromotive series is not conclusively determined. The electrical potential of uranium in contact with aqueous electrolyte has been measured by Muthmann and Fraun-

<sup>1</sup> Rideal, *loc. cit.*      <sup>2</sup> Péligré, *Ann. Chim. Phys.*, 1844, [3], 12, 557.

<sup>3</sup> Zimmermann, *Ber.*, 1882, 15, 1182.

<sup>4</sup> Rideal, *loc. cit.*; Fischer and Rideal, *Zeitsch. anorg. Chem.*, 1913, 81, 170. See also Lely, jun., and Hamburger, *ibid.*, 1914, 87, 209; Baragiola, *Chem. Zentr.*, 1916, i, 92; Schweiz, *Apoth. Zeit.*, 1915, 53, 477.

<sup>5</sup> Moissan, *Compt. rend.*, 1896, 122, 1088. See also Roderburg, *Zeitsch. anorg. Chem.*, 1913, 81, 122.

<sup>6</sup> Moore, *J. Amer. Electrochem. Soc.*, 1923, 43, 317. See also Goggins and others (*J. Ind. Eng. Chem.*, 1926, 18, 114), who reduce with metallic calcium.

<sup>7</sup> Moissan, *loc. cit.*      <sup>8</sup> Férée, *Bull. Soc. chim.*, 1901, [3], 25, 622.

<sup>9</sup> Lely, jun., and Hamburger, *loc. cit.*

<sup>10</sup> Zimmermann, *Ber.*, 1884, 17, 2739; *Annalen*, 1886, 232, 310; Péligré, *loc. cit.*

<sup>11</sup> Honda, see Wedekind, *Magnetochemie*, p. 76, Bornträger, Berlin, 1911. Meyer (*Monatsh.*, 1899, 20, 369; *Wied. Annalen*, 1899, 68, 324) gives  $+0.21 \times 10^{-6}$ .

berger,<sup>1</sup> who showed that the pure metal, in contact with a normal solution of potassium chloride, in the element



assumed a potential  $E_h = -0.46$ . The metal showed no tendency to become passive, nor does it in the usual passivating anodic solutions, though the latter may be in considerable concentration and a high current density applied.<sup>2</sup> Using an electrode of platinum on which finely powdered uranium was pasted by means of gelatin, Pierlé<sup>3</sup> obtained the following value for the metal in contact with an aqueous solution of uranyl nitrate :

$$\text{U}(91.49 \text{ per cent.})/\text{UO}_2(\text{NO}_3)_2 = -0.093 \text{ volt.}$$

By placing the metal in contact with an alcoholic solution of uranium hexachloride, Fischer and Rideal<sup>4</sup> obtained values which placed the potential of uranium between those of copper and hydrogen. This, however, is not in agreement with the above results.

The specific heat and atomic heat of the element have been determined as follows :<sup>5</sup>

Temperature, °C.	Specific Heat.	Atomic Heat.	Authority.
0	0.0276	6.57	Zimmermann, <i>Annalen</i> , 1886, <b>232</b> , 310.
0 to 98	0.0280	6.66	Blümeke, <i>Wied. Annalen</i> , 1885, <b>24</b> , 263.
-223	0.0138	3.29	Dewar, <i>Proc. Roy. Soc.</i> , 1913, A, <b>89</b> , 158.

Uranium melts at a white heat, but the exact temperature has not been determined ; Guertler and Pirani<sup>6</sup> found it to be about 1850° C., which is in agreement with a statement by Moissan that uranium is more difficult to melt than platinum. Rideal<sup>7</sup> melted in a vacuum a specimen of uranium containing 0.4 per cent. carbon ; fusion occurred between 1300° and 1400° C. The boiling-point has not been determined, but Moissan<sup>8</sup> found that the metal could be distilled more readily than iron in the electric furnace.

*Spectrum.*—Compounds of uranium do not colour a non-luminous flame. The emission spectrum is exceptionally rich in lines, which, however, are not in any way characteristic, and the detection of small quantities of uranium spectroscopically is practically impossible.<sup>9</sup> Exner and Haschek<sup>10</sup> enumerated in the arc spectrum 4940 lines between

<sup>1</sup> Muthmann and Fraunberger, *Sitzungsber. Akad. Wiss. Munich*, 1904, **34**, 214.

<sup>2</sup> Sborgi, *Atti R. Accad. Lincei*, 1912, [5], **21**, i., 135 ; *Gazzetta*, 1912, **42**, ii., 144.

<sup>3</sup> Pierlé, *J. Physical Chem.*, 1919, **23**, 517.

<sup>4</sup> Fischer and Rideal, *Zeitsch. anorg. Chem.*, 1913, **81**, 170.

<sup>5</sup> See also Donath, *Ber.*, 1879, **12**, 742.

<sup>6</sup> Guertler and Pirani, *Zeitsch. f. Metallkunde*, 1919, **11**, 1.

<sup>7</sup> Rideal, *J. Soc. Chem. Ind.*, 1914, **33**, 673.

<sup>8</sup> Moissan, *Compt. rend.*, 1906, **142**, 425.

<sup>9</sup> Russell and Rossi, *Proc. Roy. Soc.*, 1912, A, **87**, 478.

<sup>10</sup> Exner and Haschek, *Die Spectren der Elemente bei normalem Druck*, Leipzig and Wien, 1911.

the wave-lengths (Ångström units) 2263.5 and 6827.2, few of which were of marked intensity, while Kiess and Meggers<sup>1</sup> have distinguished 680 lines in the yellow, red, and infra-red, up to a wave-length of 9530 Å. Measurements have been made of the wave-lengths of the lines in the spark,<sup>2</sup> arc,<sup>3</sup> absorption,<sup>4</sup> fluorescence and phosphorescence,<sup>5</sup> and high-frequency<sup>6</sup> spectra.

Pollok<sup>7</sup> has investigated the spark spectrum of a solution of uranium chloride, with a view to determining the most *persistent* lines, and records his results as follows :<sup>8</sup>

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
4605.4	4 $\phi$	3693.9	2 $\chi$	2969.6	1 $\phi$
4603.9	$\phi$	3672.7	2 $\psi$	2941.9	2 $\chi$
4543.8	7 $\phi$	3552.4	2 $\psi$	2888.3	1 $\phi$ <sup>9</sup>
4415.4	2 $\phi$	3453.7	2 $\phi$	2865.7	2 $\chi$
4371.9	2 $\phi$	3436.9	2 $\phi$	2828.1	1 $\phi$
4355.8	4 $\phi$	3337.9	2 $\chi$	2794.0	2 $\phi$
4341.9	4 $\phi$	3270.3	2 $\phi$	2790.8	1 $\phi$
4241.9	4 $\psi$	3244.4	2 $\phi$	2766.0	1 $\phi$
4171.8	3 $\phi$	3093.1	2 $\chi$	2763.0	1 $\phi$
4090.3	4 $\chi$	3072.9	2 $\phi$	2742.7	1 $\phi$
3979.9	2 $\phi$	3058.0	2 $\chi$	2733.4	1 $\phi$
3954.9	2 $\chi$	3044.3	2 $\chi$	2635.6	2 $\chi$
3874.2	2 $\phi$	3006.9	1 $\phi$	2552.5	1 $\phi$
3859.7	2 $\phi$	2974.2	1 $\phi$	2549.5	1 $\phi$
3783.0	2 $\phi$	2971.2	2 $\phi$		

<sup>1</sup> Kiess and Meggers, *Bureau Standards Bull.*, 1920, 16, 51; *Sci. Papers*, p. 272.

<sup>2</sup> Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1909, 11, 331; Exner and Haschek, *loc. cit.*

<sup>3</sup> Thalen, *Ann. Chim. Phys.*, 1869, [4], 18, 202, 385; Hasselberg, *K. Svenska Vet.-Akad. Handl.*, 1910, 45, 3; Exner and Haschek, *loc. cit.*; Kiess and Meggers, *loc. cit.*; Meissner, *Ann. Physik*, 1916, [4], 50, 713; Meyer, *Physikal. Zeitsch.*, 1921, 22, 583; *Discovery*, 1921, p. 585.

<sup>4</sup> Morton and Bolton, *Chem. News*, 1873, 28, 47, 113, 164; Vogel, *Ber.*, 1875, 8, 1535; 1878, 11, 915; Zimmermann, *Annalen*, 1882, 213, 285; Becquerel, *Compt. rend.*, 1907, 144, 459; Jones and Strong, *Phil. Mag.*, 1910, [6], 19, 566; *Amer. Chem. J.*, 1911, 45, 1, 113; Strong, *Physikal. Zeitsch.*, 1910, 11, 668; Mazzucchelli and d'Alceo, *Atti R. Accad. Lincei*, 1912, [5], 21, ii, 850; 1913, [5], 22, i, 41; Mazzucchelli and Perret, *ibid.*, 1913, [5], 22, ii, 445; Jones and Guy, *Amer. Chem. J.*, 1913, 49, 1; Morton, *Proc. Roy. Soc.*, 1912, A, 87, 138; *Proc. Chem. Soc.*, 1913, 29, 284; *Trans. Chem. Soc.*, 1914, 105, 23; Henri and Landau, *Compt. rend.*, 1914, 158, 181; Howes, *Phys. Review*, 1918, [2], 11, 66, 143; Nichols and Howes, *ibid.*, 1919, [2], 14, 293; Moir, *Trans. Roy. Soc. S. Africa*, 1919, 8, 45; 1921, 10, 33; Dauvillier, *J. phys. Radium*, 1922, 3, 221.

<sup>5</sup> E. Becquerel, *Ann. Chim. Phys.*, 1872, [4], 27, 539; *Compt. rend.*, 1879, 88, 1237; H. Becquerel, *ibid.*, 1885, 101, 1252; 1907, 144, 459; Cantoni, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1907, [3], 13, 149; Nichols and Howes, *loc. cit.*; Becquerel and Kamerlingh-Onnes, *Compt. rend.*, 1910, 150, 647.

<sup>6</sup> Siegbahn, *Ber. Deut. physikal. Ges.*, 1916, 18, 150, 278; Siegbahn and Friman, *Physikal. Zeitsch.*, 1916, 17, 17, 61; *Phil. Mag.*, 1916, [6], 32, 39; Dauvillier, *Compt. rend.*, 1921, 172, 1350; de Broglie and de Broglie, *ibid.*, 1921, 173, 527; de Broglie, *ibid.*, 1922, 174, 939; Dolejšek, *Zeitsch. Physik*, 1922, 10, 129; *Nature*, 1922, 109, 582.

<sup>7</sup> Pollok, *loc. cit.*

<sup>8</sup> For a general description of the method, and explanation of the abbreviations employed, see pp. 13, 14.

<sup>9</sup> Triple line, of which only one wave-length is given.



Exner and Haschek (*loc. cit.*) record the following as the most intense lines in the arc and spark spectra of uranium :

Arc Spectrum.		Spark Spectrum.	
Wave-length.	Intensity.	Wave-length.	Intensity.
3932.19	5	4090.28	4
4090.26	5	4241.88	4
4171.74	5	4269.84	4
4341.83	5	4341.89	4
4355.82	5	4355.89	4
5493.15	10	4472.55	6
5528.01	10	4515.50	4
5915.61	8	4543.79	7
6395.68	8	4545.76	4
6449.38	10	4555.30	4
		4603.86	4
		4627.26	5
		4646.80	4
		4689.28	4
		5493.16	4
		5528.02	4

Owing to the fact that 7.5 per cent. of the principal uranium lines are absent from the solar spectrum, it has been suggested<sup>1</sup> that this element is probably absent from the sun, but Meyer<sup>2</sup> has shown that in presence of other metals the emission spectrum of uranium is invisible, unless the latter element is present in considerable concentration, usually about 7 per cent., and this worker therefore suggests that the absence of uranium lines in the solar spectrum is due to the presence of relatively large quantities of iron.

**Chemical Properties.** Metallic uranium exhibits considerable chemical activity. Although unchanged at ordinary temperatures in dry air, the brightly polished metal becomes considerably tarnished after a few days exposure to the atmosphere ;<sup>3</sup> it burns briskly at 170° C.,<sup>4</sup> forming uranous oxide. It burns in sulphur vapour at 500° C., and also in selenium vapour. The halogens react vigorously ; the metal inflames immediately in fluorine in the cold, in chlorine at 180° C., in bromine at 210° C., and in iodine vapour at 260° C. Dry hydrogen chloride and hydrogen iodide attack at a dull red heat. Nitrogen combines at 1000° C. to produce a yellow nitride, and the metal decomposes ammonia, liberating hydrogen and yielding a black crystalline powder. With carbon the metal yields a well-defined crystalline carbide. According to Moissan, finely divided uranium readily decomposes water ; Lely and Hamburger,<sup>5</sup> however, found the metal stable towards water

<sup>1</sup> Hasselberg, *K. Svenska Vet.-Akad. Handl.*, 1910, 45, 3.

<sup>2</sup> Meyer, *Physikal. Zeitsch.*, 1921, 22, 583.

<sup>3</sup> Moore, *J. Amer. Electrochem. Soc.*, 1923, 43, 323.

<sup>4</sup> Moissan, *Compt. rend.*, 1896, 122, 1088.

<sup>5</sup> Lely, jun., and Hamburger, *Zeitsch. anorg. Chem.*, 1914, 87, 200.

and towards alkalis. Dilute hydrochloric and sulphuric acids dissolve uranium with vigorous evolution of hydrogen; concentrated sulphuric acid yields sulphur dioxide; nitric acid forms the nitrate. Uranium displaces the following metals, in part even in the cold, from solutions of their salts: mercury, silver, copper, tin, platinum, and gold.

**Pyrophoric Uranium.**—It has already been mentioned (p. 278) that uranium, in a very finely divided condition, takes fire on exposure to air. The black powder obtained by reduction of the oxide by means of magnesium exhibits this property. Chesneau observed<sup>1</sup> that the sparks detached from uranium by friction with hard steel would ignite mixtures of methane and air, as well as such inflammable liquids as alcohol and benzene, and he concluded that their temperature could not be below 1000° C. The product obtained by Ferée (see p. 279) by heating uranium amalgam *in vacuo* burned spontaneously in the air. Alloys of uranium and iron containing more than 20 per cent. of uranium are pyrophoric,<sup>2</sup> the activity increasing with increase in uranium content.

**Colloidal Uranium.**—Uranium has been obtained in colloidal form by means of dispersion methods,<sup>3</sup> but the sols do not appear to be stable for more than a few hours. Svedberg prepared by electrical dispersion the *isobutyl* alcosol, which was deep brown by transmitted light and black by reflected light, and was completely coagulated after standing twelve hours.

**Atomic Weight.**—The earlier investigations<sup>4</sup> into the atomic weight of uranium are of little more than historic interest, owing in the first place to the erroneous idea that the oxide was the element (see p. 276), and also to the fact that the analytical results obtained were often widely discordant, probably due to the impure nature of the materials studied. The valency of the element was assumed to be 3 and the atomic weight appeared to be about 120. After the recognition of the true nature of the oxide and the isolation of the metal, Péligot<sup>5</sup> made a series of analyses of the oxalate and acetate of uranium, and from his results the atomic weight 120 (O=16) was again obtained.

In 1872 Mendeléeff<sup>6</sup> pointed out that there was no place in the Periodic Table for a trivalent element of atomic weight 120, and drew attention to the similarity of uranium to chromium, molybdenum, and tungsten; he therefore suggested that the atomic weight should be doubled, so that uranium could be placed below these elements in the table. He also formulated the oxides, by analogy with those of the other elements in the group, as follows: uranous oxide  $\text{UO}_2$ , urano-

<sup>1</sup> Chesneau, *Compt. rend.*, 1896, 122, 471.

<sup>2</sup> Polushkin, *Iron and Steel Inst., Carnegie Schol. Mem.*, 1920, 10, 129; *Revue de Métallurgie*, 1920, 17, 421.

<sup>3</sup> Kužel, *German Patent*, 186980 (1907); Svedberg, *Herstellung Kolloider Lösungen anorganischer Stoffe*, Dresden, 1909; Agulhon and Robert, *Compt. rend.*, 1914, 158, 349.

<sup>4</sup> Schönberg, *Schweigger's J.*, 1815, 15, 284; *De conjunctione chemici ejusque rationibus*, Upsala, 1813; Arfvedson, *Pogg. Annalen*, 1823, 1, 254; Berzelius, *Jahresber.*, 1824, 22, 113; *Pogg. Annalen*, 1825, 1, 359; Péligot, *Compt. rend.*, 1841, 12, 735; *Ann. Chim. Phys.*, 1841, [3], 5, 12; *J. prakt. Chem.*, 1841, 23, 404; Marchand, *ibid.*, 1841, 23, 497; Ebelmen, *Ann. Chim. Phys.*, 1842, [3], 5, 189; *Annalen*, 1842, 43, 286; Rammelsberg, *Pogg. Annalen*, 1842, 55, 318; 1842, 56, 125; 1843, 59, 9; 1845, 66, 91; Wertheim, *Ann. Chim. Phys.*, 1844, [3], 11, 49; *J. prakt. Chem.*, 1843, 29, 209.

<sup>5</sup> Péligot, *Compt. rend.*, 1846, 22, 487; *J. prakt. Chem.*, 1846, 38, 112; *Ann. Chim. Phys.*, 1847, [3], 20, 329.

<sup>6</sup> Mendeléeff, *Annalen Suppl.*, 1872, 8, 178; *Chem. News*, 1880, 41, 39.

uranic oxide  $\text{U}_3\text{O}_8$  or  $\text{UO}_2 \cdot 2\text{UO}_3$ , uranic oxide  $\text{UO}_3$ ; thus suggesting that the element was both tetra- and hexa-valent. The correctness of these suggestions was confirmed by the determination of the specific heat of the metal<sup>1</sup> and the application of Dulong and Petit's Law, and also by vapour-density determinations of uranous chloride and bromide,<sup>1</sup> and later of uranic fluoride.<sup>2</sup>

In 1902 Richards and Merigold<sup>3</sup> analysed uranous bromide, and determined the bromine as silver bromide. The uranous bromide was carefully purified by sublimation in an atmosphere of either bromine or nitrogen, oxygen being rigorously excluded. The operations, however, were carried out in glass vessels, and a correction had to be made for the presence of a small amount of sodium bromide in the uranous bromide. A further source of error, namely, that at the high temperature of sublimation the uranous bromide reacts with the glass to form small quantities of the oxybromide  $\text{UO}_2\text{Br}_2$ , was not taken into account, so that the values obtained must be considered too high. The vessel, containing a known weight of the uranous bromide, was opened under water, dilute hydrogen peroxide added, and the bromine precipitated in one series of experiments by excess of silver nitrate, and in another series by the addition of the exact weight of silver dissolved in nitric acid. The results were as follows: <sup>4</sup>

4 expts.	. $\text{UBr}_4 : 4\text{AgBr} :: 74.2908 : 100.0000$ , whence $\text{U} = 238.4$ .
3 „	. $\text{UBr}_4 : 4\text{AgBr} :: 74.2960 : 100.0000$ , „ $\text{U} = 238.4$ .
3 „	. $\text{UBr}_4 : 4\text{Ag} :: 129.3280 : 100.0000$ , „ $\text{U} = 238.4$ .

In 1914 Hönigschmid<sup>5</sup> repeated the experiments of Richards and Merigold, using apparatus of silica. Uranous bromide was carefully purified by sublimation either in bromine vapour or in nitrogen, and the product was then melted and transferred to a silica weighing-tube in absence of air. The ratio  $\text{UBr}_4 : 4\text{AgBr}$  was estimated gravimetrically, and the  $\text{UBr}_4 : 4\text{Ag}$  by titration. The results were as follows ( $\text{Ag} = 107.880$ ,  $\text{Br} = 79.916$ ):

(1) After sublimation in bromine,

8 expts.	. $\text{UBr}_4 : 4\text{AgBr} :: 74.24803 : 100.00000$ , whence $\text{U} = 238.09$ .
6 „	. $\text{UBr}_4 : 4\text{Ag} :: 129.2547 : 100.0000$ , „ $\text{U} = 238.11$ .

(2) After sublimation in nitrogen,

14 expts.	. $\text{UBr}_4 : 4\text{AgBr} :: 74.26192 : 100.00000$ , whence $\text{U} = 238.19$ .
9 „	. $\text{UBr}_4 : 4\text{Ag} :: 129.2722 : 100.0000$ , „ $\text{U} = 238.18$ .

The lower values obtained in the former experiments were due to adsorption of traces of bromine during sublimation, and the values

<sup>1</sup> Zimmermann, *Annalen*, 1882, 216, 1.

<sup>2</sup> Ruff and Heinzelmann, *Zeitsch. anorg. Chem.*, 1911, 72, 63.

<sup>3</sup> Richards and Merigold, *Proc. Amer. Acad.*, 1902, 37, 395; *Zeitsch. anorg. Chem.*, 1902, 31, 235. Earlier data are those of Zimmermann (*Annalen*, 1886, 232, 299),  $\text{U} = 239.6$ , and Aloy (*Ann. Chim. Phys.*, 1901, [7], 24, 418),  $\text{U} = 237$ .

<sup>4</sup> Assuming the following fundamental values:  $\text{Ag} = 107.880$ ;  $\text{O} = 16.000$ ;  $\text{Br} = 79.916$ , Lebeau (*Compt. rend.*, 1912, 155, 163), from the ratio  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} : \text{UO}_2$ , obtained the value  $\text{U} = 238.55$ . O. de Coninck (*Bull. Acad. roy. Belg.*, 1907, p. 1041; 1908, pp. 163, 1477; *Compt. rend.*, 1908, 152, 711, 1179; 1912, 155, 1511) reduced uranyl chloride and bromide, but failed to obtain concordant results.

<sup>5</sup> Hönigschmid, *Compt. rend.*, 1914, 158, 2004; *Zeitsch. Elektrochem.*, 1914, 20, 452; *Monatsh.*, 1915, 36, 355.

from the second series of experiments are more reliable. For these researches, the uranium salt was derived from minerals obtained from the Joachimsthal deposits, the age of which is estimated to be 250 million years; in order to see if the atomic weight of uranium, which is considered to be a mixture of two isotopes (see below), varied with the age of the mineral, Hönigschmid and Horovitz<sup>1</sup> made further experiments, the methods being precisely as above, but the uranium was obtained from a very pure crystalline form of uraninite from Morogoro in East Africa, the age of which is about 800 million years. The results were as follows:

(1) After sublimation in bromine,

4 expts. .  $\text{UBr}_4 : 4\text{AgBr} :: 74.24378 : 100.00000$ , whence  $\text{U} = 238.05$ .  
 4 „ .  $\text{UBr}_4 : 4\text{Ag} :: 129.2450 : 100.0000$ , „  $\text{U} = 238.06$ .

(2) After sublimation in nitrogen,

5 expts. .  $\text{UBr}_4 : 4\text{AgBr} :: 74.25872 : 100.00000$ , whence  $\text{U} = 238.16$ .  
 5 „ .  $\text{UBr}_4 : 4\text{Ag} :: 129.2702 : 100.0000$ , „  $\text{U} = 238.17$ .

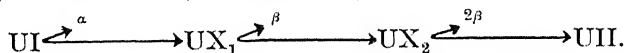
These results are identical with those of the earlier experiments, and as before the higher results are more correct.

This work is the most reliable done up to the present (January 1926), and the true atomic weight appears to be slightly below 238.2. The International Committee for 1925 accept the value

$$\text{U} = 238.17.$$

Uranium is thus the terminal member of the periodic system, possessing a greater atomic mass than any other known element.

**Isotopes of Uranium.**—Ordinary uranium is a mixture of two isotopes, uranium I and uranium II, whose atomic weights differ by 4, the weight of one  $\alpha$ -particle which is ejected by an atom of the former according to the following scheme (see p. 342):



The isotopes are inseparable and chemically identical. The atomic weight of ordinary uranium, found by the methods above described, must therefore be considered as a mean value of the atomic weights of uranium I and uranium II, depending upon the proportions of each present. It was this consideration that led Hönigschmid to use in his investigations specimens of uranium ores whose ages were estimated as 250 million and 800 million years respectively. The fact that the atomic weights determined from these experiments were identical within experimental error indicated that the ratio UI : UII in the two sources was not appreciably different. It is probable that the amount of uranium II present in uranium is very small, at most 0.04 per cent., since the half-life (see p. 342) of uranium I is very great,  $5 \times 10^9$  years, and only a little uranium II can form by way of the short-lived elements uranium  $\text{X}_1$  and uranium  $\text{X}_2$ ; whilst the comparatively short half-life of uranium II,  $2 \times 10^6$  years, would prevent any considerable accumulation of uranium II. Thus the difference between the atomic weight of uranium I and the value given above as the atomic weight of uranium is unimportant, being within the analytical error.

<sup>1</sup> Hönigschmid and Horovitz, *Monatsh.*, 1916, 37, 185.

**Alloys of Uranium.**—Alloys of uranium and aluminium are readily obtained by the addition of a mixture of urano-uranic oxide and aluminium powder to a bath of molten aluminium; <sup>1</sup> by heating a mixture of uranic oxide and aluminium by the aluminothermic process; <sup>2</sup> or by electrolysis of the fused double chloride,  $K_2UCl_6$ , using aluminium electrodes.<sup>3</sup> By the aluminothermic process, Guillet obtained products of definite composition:  $U_2Al_3$ , hard lustrous cubic crystals, and  $UAl_3$ , fine needle-shaped crystals.

Many alloys of uranium and iron, containing up to 70 per cent. of uranium, have been obtained by reduction of uranium oxide with carbon and iron. After purification, the alloys contain about 2 per cent. of carbon, silicon, vanadium, and sometimes aluminium. Ferro-uranium alloys with more than 20 per cent. uranium exhibit pyrophoric properties which increase with increasing content of uranium.<sup>4</sup> In Colorado the alloys are obtained as by-products in the extraction of radium from carnotite, and contain 35 to 40 per cent. of uranium and 1.5 to 4 per cent. of carbon. If less than 2 per cent. of carbon is present the alloys are tough, but with more carbon they are brittle; the presence of silicon increases the brittleness. The carbon is usually present as carbides of uranium, iron, and vanadium, and such alloys are decomposed by water. Uranium does not form solid solutions with iron.<sup>5</sup> Uranium steels containing ferro-uranium of low carbon content possess similar properties to tungsten steels (see p. 191).

According to Stavenhagen and Schuchard<sup>6</sup> the following alloys have been prepared by the method of aluminothermic reduction:  $UFe$ ,  $UMn$ ,  $UFeMn$ ,  $UCo$ ,  $UMo$ , and  $UMoCrTi$ .

Uranium combines with arsenic and antimony to form definite compounds (see pp. 332, 333).

<sup>1</sup> Moissan, *Compt. rend.*, 1896, 122, 1302.

<sup>2</sup> Guillet, *Bull. Soc. d'encourag.*, 1902, 101, ii., 254.

<sup>3</sup> Aloy, *Ann. Chim. Phys.*, 1901, [7], 24, 412; *Recherches sur l'Uranium et ses composés*, Thesis 21, Paris, 1901, p. 14.

<sup>4</sup> Gillet and Mack, *J. Ind. Eng. Chem.*, 1917, 9, 342; Gillet, *Bull. Amer. Inst. Mining Engineers*, 1918, 140, 1653; *Engineering*, 1918, 105, 41; *Chem. Zentr.*, 1918, i., 311; 1919, i., 213; 1919, ii., 574; Keeney, *Eng. and Min. J.*, 1918, 106, 405; *Bull. Amer. Inst. Mining Engineers*, 1918, 140, 1321; *Chem. Zentr.*, 1919, ii., 573; Polushkin, *Iron and Steel Inst., Carnegie Schol. Mem.*, 1920, 10, 129; *Revue de Métallurgie*, 1920, 17, 421.

<sup>5</sup> Polushkin, *loc. cit.*

<sup>6</sup> Stavenhagen and Schuchard, *Ber.*, 1902, 35, 909.

## CHAPTER IX.

### COMPOUNDS OF URANIUM.

#### GENERAL PROPERTIES OF URANIUM COMPOUNDS.

URANIUM is the terminal member of the chromium group of elements, and in its chemical behaviour it shows considerable resemblance to the other members of the group.<sup>1</sup> Like them it exhibits valency varying from 2 to 6, but it is most stable in the hexavalent condition. The trioxide,  $\text{UO}_3$ , like the trioxides of molybdenum and tungsten, is amphoteric, but the acidic qualities are less evident. It forms on the one hand a hexafluoride,  $\text{UF}_6$ , and a large group of uranyl salts of the type  $\text{UO}_2\text{X}_2$ , where X is a monovalent electronegative element or radical; and on the other, stable uranates corresponding to acids of composition  $\text{H}_2\text{UO}_4$  and  $\text{H}_2\text{U}_2\text{O}_7$ . It does not, however, tend to the formation of complex heteropolyacids in any marked degree. The uranyl salts, which contain the uranyl group  $\text{UO}_2$  as a divalent metallic radical, may be regarded as stable intermediate products of the hydrolytic decomposition of the normal salts of hexavalent uranium. They are well-defined crystalline salts, generally yellow, although the presence of certain organic groups in the molecule may displace the colour strongly towards the red;<sup>2</sup> both in the crystalline form and in solution they exhibit a greenish fluorescence.<sup>3</sup> They are somewhat analogous to basic salts, but are stable in solution and little hydrolysed. They enter into combination with other salts, especially those of organic acids, and form numerous stable complexes of well-defined crystalline form. Of the normal uranic salts only the hexafluoride is known.

The uranous compounds correspond to the basic oxide,  $\text{UO}_2$ , and are usually green or blue in colour. They may be prepared by reduction of uranyl salts in solution under the influence of light (see below), but they are the more unstable and the solutions are readily oxidised back by air to uranyl compounds, especially in the presence of platinum black or of salts of iron or copper.<sup>4</sup> In the uranous compounds uranium shows considerable chemical similarity to thorium, the terminal member of Group IV (see p. 4).

The intermediate oxide,  $\text{U}_3\text{O}_8$ , which appears to contain both tetra- and hexa-valent uranium, does not yield a corresponding series of salts. A large number of violet precipitates have, however, been obtained from solutions containing uranous and uranic salts present together, all of

<sup>1</sup> Mendeléeff, *Annalen Suppl.*, 1872, 8, 178; *Chem. News*, 1880, 41, 39; O. de Coninck, *Bull. Acad. roy. Belg.*, 1909, p. 175.

<sup>2</sup> Müller, *Zeitsch. anorg. Chem.*, 1919, 109, 239.

<sup>3</sup> See Nichols, Howes, Merritt, Wilber, and Wick, *Carnegie Inst. Washington Publication*, 1919, 298, 1, on the fluorescence of uranyl salts.

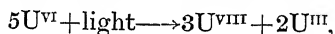
<sup>4</sup> Luther and Michie, *Zeitsch. Elektrochem.*, 1908, 14, 826.

which, by loss of their acid radical, tend to become transformed into the green hydrated oxide,  $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ .<sup>1</sup>

In addition to the derivatives of the oxides,  $\text{UO}_2$  and  $\text{UO}_3$ , uranium forms a few compounds in which it appears to exhibit valencies equal to 5, 3, and possibly 2. It yields, for example, a comparatively stable pentachloride,  $\text{UCl}_5$ , and a much less stable trichloride,  $\text{UCl}_3$ . It produces a variety of sulphides:  $\text{US}$ ,  $\text{U}_2\text{S}_3$ ,  $\text{US}_2$ ,  $\text{UO}_2\text{S}$ , but it does not show the tendency found in molybdenum and tungsten to form soluble sulpho-salts.

It forms a peracid,  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ , which shows considerable activity towards metallic peroxides, with the production of a well-defined series of peruranates.

**Influence of Light on Uranium Compounds.**—It has already been mentioned that uranyl salts in solution exhibit a greenish fluorescence.<sup>2</sup> If the solutions are exposed to light in the presence of readily oxidisable organic substances, such as alcohol, reduction takes place, uranous salts being formed. At the same time the fluorescence disappears, the uranous salts not exhibiting this property. This reduction under the influence of light is known as *photolysis*, and has been the subject of much investigation.<sup>3</sup> The action is accelerated by the presence of substances which destroy fluorescence, and the two phenomena appear to be connected.<sup>4</sup> It has been suggested by Baur<sup>5</sup> that when light is absorbed by the uranyl ion, the uranium assumes a more active condition. If any substance is present with which the active uranium can react, it does so, and suffers reduction; but if not, the reverse reaction takes place, with emission of fluorescence. Baur further suggests that during absorption of light the hexavalent uranium is resolved into octavalent and trivalent uranium thus:



and that, as the absorbed energy is given off in the form of fluorescence, the reverse reaction occurs, the hexavalent uranium being again produced. This reverse reaction, however, is prevented from taking place by the presence of substances which destroy fluorescence; these are generally either reducing agents, such as oxalic acid, potassium iodide, or uranous salts, which might be expected to destroy any salts of octavalent uranium; or oxidising agents, such as ferric salts, which would

<sup>1</sup> Aloy, *Bull. Soc. chim.*, 1900, [3], 23, 368; Aloy and Rodier, *ibid.*, 1920, [4], 27, 101.

<sup>2</sup> The emission and absorption spectra, and phosphorescence at low temperatures, have been studied by E. Becquerel, *Ann. Chim. Phys.*, 1872, [4], 27, 539; H. Becquerel, *Compt. rend.*, 1907, 144, 671; H. Becquerel, J. Becquerel, and Onnes, *ibid.*, 1910, 150, 647; Morton and Bolton, *American Chemist*, 1872, iii., 361, 401.

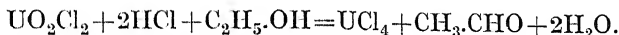
<sup>3</sup> Bucholtz, *Ann. Chim. Phys.*, 1806, [1], 56, 142; Bonaparte, *J. prakt. Chem.*, 1843, [1], 30, 308; Burnett, *Liverpool Journ. Phot.*, 1857; Niepce and Corvisart, *Compt. rend.*, 1859, 49, 370; *Annalen*, 1860, 113, 114; Seekamp, *ibid.*, 1862, 122, 115; 1865, 133, 253; 1893, 278, 373; Bolton, *Amer. J. Sci.*, 1869, [2], 48, 206; Chastaing, *Ann. Chim. Phys.*, 1877, [5], 11, 145; Ostwald, *Zeitsch. physikal. Chem.*, 1888, 2, 127; Wisbar, *Annalen*, 1891, 262, 232; Bach, *Compt. rend.*, 1893, 116, 1145; Fay, *Amer. Chem. J.*, 1896, 18, 269; Jorissen, *Zeitsch. angew. Chem.*, 1899, 12, 521; Jorissen and Reicher, *Zeitsch. physikal. Chem.*, 1899, 31, 142; Ruff, *Ber.*, 1901, 34, 3509; Euler, *ibid.*, 1904, 37, 3411; Usher and Priestley, *Proc. Roy. Soc.*, 1906, 78, 318; Plotnikow, *Zeitsch. physikal. Chem.*, 1907, 58, 214; Luther and Plotnikow, *ibid.*, 1908, 61, 513.

<sup>4</sup> Baur, *Helv. Chim. Acta*, 1918, 1, 186; Hatt, *Zeitsch. physikal. Chem.*, 1918, 92, 513; Baur, *Zeitsch. Elektrochem.*, 1919, 25, 102; Baur and Rebmann, *Helv. Chim. Acta*, 1922, 5, 221; Baur and Haggemacher, *Zeitsch. physikal. Chem.*, 1922, 100, 36.

<sup>5</sup> Baur, *Schweiz. Chem. Zeit.*, 1918, 2, 40.

react with salts of trivalent uranium. In the decomposition of oxalic acid by means of uranyl sulphate under the influence of light, carbon monoxide and carbon dioxide are evolved, and the trivalent uranium compounds react with unchanged hexavalent uranium, forming products in an intermediate stage of oxidation. A small quantity of formic acid is found in the solution, but this is unable to accumulate since it is used up in reducing the uranyl-ion to uranous-ion.<sup>1</sup> The final product of the reduction of uranyl oxalate is a violet hydrated form of urano-uranic oxide.<sup>2</sup>

Many oxidation and reduction reactions, especially in organic chemistry, are in consequence considerably influenced by the presence of uranyl salts under the action of light.<sup>3</sup> The reaction may also be used as a means of preparing uranous salts,<sup>4</sup> by exposing to light a solution of the uranyl salt containing the requisite quantity of the acid entering into the constitution of the salt, and a readily oxidisable substance such as alcohol. In the case of the chloride the reaction is as follows :



If insufficient acid is added, basic salts result; while if the reaction is allowed to proceed further, a black precipitate of uranous hydroxide is obtained.

**Photoelectric Cells.**—A noteworthy effect which appears to be in some way connected with photolysis was discovered by Baur,<sup>5</sup> who observed that the potential difference at a platinum electrode immersed in a solution containing both uranyl and uranous salts was considerably less positive when exposed to sunlight than when kept in the dark. If two platinum electrodes are immersed in a solution of the mixed salts, and it is arranged so that one electrode is exposed to a bright light while the other is kept in the dark, the cell can be made to furnish a current.<sup>6</sup> The displacement of potential appears to be due to changes which occur in the uranyl salt under the influence of light, possibly with formation of pentavalent and octavalent uranium.<sup>7</sup> The effect is weakened by the presence of those substances which inhibit the fluorescence of uranyl compounds (see above).<sup>8</sup>

Many uranium salts, like other fluorescent and phosphorescent substances, are triboluminescent—that is, they emit light when crushed<sup>9</sup> (see p. 324).

**Electrochemical Behaviour.**—The electrolysis of solutions containing uranium compounds has not been fully investigated, but in general the product at the cathode appears to consist of hydrated oxides in various stages of oxidation.<sup>10</sup> This is the case even when a

<sup>1</sup> Baur and Haggemacher, *loc. cit.*

<sup>2</sup> Courtois, *Bull. Soc. chim.*, 1923, 33, iv., 1773.

<sup>3</sup> Bacon, *Philippine J. Sci.*, 1907, 2, 129; Berthelot and Gaudechon, *Compt. rend.*, 1911, 152, 262; 1913, 157, 333; Aloy and Valdiguié, *ibid.*, 1923, 176, 1229; *Bull. Soc. chim.*, 1923, [4], 33, 572.

<sup>4</sup> Aloy and Rodier, *Bull. Soc. chim.*, 1922, [4], 31, 246.

<sup>5</sup> Baur, *Zeitsch. physikal. Chem.*, 1908, 63, 683; 1910, 72, 323; 1912, 80, 668.

<sup>6</sup> Titlestad, *Zeitsch. physikal. Chem.*, 1910, 72, 257; Trümpler, *ibid.*, 1915, 90, 385.

<sup>7</sup> Trümpler, *loc. cit.*

<sup>8</sup> See also Goldmann, *Ann. Physik*, 1908, [4], 27, 449; Samsonow, *Zeitsch. wiss. Photochem.*, 1910, 9, 12; Schiller, *Zeitsch. physikal. Chem.*, 1912, 80, 641.

<sup>9</sup> Siemssen, *Chem. Zeit.*, 1919, 43, 267; 1922, 46, 450.

<sup>10</sup> Smith, *Ber.*, 1880, 13, 751; Kollock and Smith, *J. Amer. Chem. Soc.*, 1901, 23, 607; Fischer and Rideal, *Zeitsch. anorg. Chem.*, 1913, 81, 170.



diaphragm is used. The metal itself is not deposited under ordinary conditions (compare p. 279). According to Pierlé,<sup>1</sup> on electrolysing aqueous solutions of uranyl salts with low-current density, the first product is hydrated uranic oxide,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ , which gradually changes, as electrolysis proceeds, to a black oxide of varying composition. With higher current density, uranyl sulphate is reduced to uranous sulphate, and if the solution is neutral or alkaline, a mixture of black and yellow oxides is deposited; in acid solution, only a slight deposit, metallic in appearance, is obtained. A concentrated solution of uranyl nitrate gives a black pyrophoric substance of undetermined composition, which, when dried and heated, yields a product of composition  $\text{U}_2\text{O}_5$ .<sup>2</sup> When uranous salts are electrolysed, a black deposit, of composition  $\text{U}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ , is obtained at the cathode.<sup>3</sup>

The method of electrolysis has been suggested<sup>4</sup> as a means of separating uranium from solutions of uranyl salts, the hydrated oxide deposited being converted by heat to the oxide,  $\text{U}_3\text{O}_8$ .

The electrolysis of uranium compounds in organic solvents has been investigated.<sup>5</sup>

Uranyl salts in solution undergo hydrolysis, and the electrical conductivity of such solutions increases with time. The difference between  $\Lambda_{32}$  and  $\Lambda_{1024}$  for many of the salts (see pp. 296, 320, 325) is abnormally high, probably because the dissociation takes place in stages.<sup>6</sup>

**Physiological Action.**—Uranium in its soluble compounds behaves as a strong poison towards the animal organism,<sup>7</sup> causing acute gastric inflammation.<sup>8</sup> In dilute solution uranium salts inhibit the development of bacteria, unless in exceedingly minute concentration when growth may be stimulated;<sup>9</sup> also, if absorbed by the roots of higher plants, growth is arrested.<sup>10</sup>

**Radioactivity.**<sup>11</sup>—This is discussed in Chapter X.

**Uses.**—Uranium compounds are produced as by-products in the extraction of radium, and are consequently available in considerable quantity. They are not, however, as yet employed in industry to any great extent. Sodium uranate, or uranium yellow, is used to a limited extent for colouring glass, to which it imparts a yellow opalescence, and in the ceramic industries, as also is the oxide  $\text{U}_3\text{O}_8$  in the preparation of yellow, brown, and green glazes.<sup>12</sup> Certain salts are employed

<sup>1</sup> Pierlé, *J. Physical Chem.*, 1919, 23, 517.

<sup>2</sup> O. de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, p. 321.

<sup>3</sup> Pierlé, *loc. cit.* Cf. Smith, *Amer. Chem. J.*, 1879, 1, 329.

<sup>4</sup> Kollock and Smith, *J. Amer. Chem. Soc.*, 1901, 23, 607; Wherry and Smith, *ibid.*, 1907, 29, 806.

<sup>5</sup> Pierlé, *loc. cit.*

<sup>6</sup> Dittrich, *Zeitsch. physikal. Chem.*, 1899, 29, 449.

<sup>7</sup> Leconte, *Gazette méd. de Paris*, 1854, p. 196.

<sup>8</sup> Chittenden and Lambert, *Zeitsch. Biol.*, 1889, 25, 513; Worochilsky, *Chem. Zeit.*, 1890, 14, 1002; Fleckseder, *Arch. exp. Pathol. Pharmacol.*, 1906, 56, 54; Jackson, *Amer. J. Physiol.*, 1910, 26, 381; Jackson and Mann, *Indiana Univ. Studies*, 1911, 8, 2.

<sup>9</sup> Kayser, *Compt. rend.*, 1912, 155, 246; Agulhon and Sazerac, *Bull. Soc. chim.*, 1912, [4], 11, 868; *Compt. rend.*, 1912, 155, 1186; 1913, 156, 162; Agulhon and Robert, *ibid.*, 1914, 158, 349; P. Becquerel, *ibid.*, 1913, 156, 164; Lepierre, *ibid.*, 1913, 156, 1179; *Bull. Soc. chim.*, 1913, [4], 13, 491.

<sup>10</sup> Loew, *Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 5, 173; *Chem. Zentr.*, 1902, ii., 1331; Acqua, *ibid.*, 1912, ii., 1471; *Atti R. Accad. Lincei*, 1913, [5], 22, ii., 390; Stoklasa, *Compt. rend.*, 1913, 156, 153.

<sup>11</sup> The phenomenon of radioactivity is discussed in detail in Vol. III., Part I., of this series.

<sup>12</sup> Riddle, *Trans. Amer. Ceram. Soc.*, 1906, 8, 210; Minton, *ibid.*, 1907, 9, 771.

as mordants in the dyeing of wool and silk,<sup>1</sup> and their use has been suggested for the production of brown colours.<sup>2</sup> In photography, uranium salts are used to a small extent.<sup>3</sup> The use of uranium carbide as a catalyst in the synthetic production of ammonia has been suggested. Attempts have also been made to make use of the metal in illumination, in ways similar to those in which tungsten and other high melting metals have been employed;<sup>4</sup> also to make use of the pyrophoric properties of uranium, and to develop the production of uranium steels. Such attempts, however, have not as yet proceeded very far.

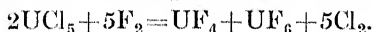
#### URANIUM AND HYDROGEN.

No compound of uranium with hydrogen has been obtained.

#### URANIUM AND FLUORINE.

**Uranium Difluoride, UF<sub>2</sub>.**—The solution obtained after electrolysis of an aqueous solution of uranyl chloride acidified with hydrochloric acid yields, on addition of excess of hydrofluoric acid, a green precipitate of composition UF<sub>2</sub>·2H<sub>2</sub>O.<sup>5</sup>

**Uranium Tetrafluoride, Uranous Fluoride, UF<sub>4</sub>,** is the chief product obtained when the metal is acted upon by fluorine. It may be prepared by the action of hydrogen fluoride on urano-uranic oxide<sup>6</sup> or on uranous oxide;<sup>7</sup> or by reduction of a solution of uranyl fluoride with stannous chloride.<sup>8</sup> It is also formed with uranium hexafluoride when the pentachloride is acted upon by fluorine at  $-40^{\circ}$  C.<sup>9</sup> thus :



The hexafluoride may be removed by distillation. Dry hydrogen fluoride acts in a similar manner (see below). Uranium carbide, UC<sub>2</sub>, reacts with pure fluorine to yield the tetrafluoride only.

Uranous fluoride is a green amorphous powder, insoluble in water, hardly attacked by dilute acids and only dissolved with difficulty by concentrated acids, except in the case of nitric acid which readily decomposes it. When heated in the air it loses fluorine and leaves a residue of urano-uranic oxide. At ordinary temperatures it is gradually oxidised to the uranyl compound, UO<sub>2</sub>F<sub>2</sub>. If heated in absence of air it melts at about  $1000^{\circ}$  C.<sup>9</sup>

The insolubility of uranous fluoride affords a method of estimating the metal by precipitation with hydrofluoric acid.<sup>10</sup>

The monohydrate, UF<sub>4</sub>·H<sub>2</sub>O, is obtained<sup>8</sup> by drying at  $100^{\circ}$  C. the

<sup>1</sup> Odernheimer, *Färber-Zeitung*, 1894, 5, 17; *German Patent*, 72523 (1892).

<sup>2</sup> Werner, *Bull. Soc. ind. Mulhouse*, 1892, p. 542.

<sup>3</sup> Roche, *J. Soc. Chem. Ind.*, 1888, 7, 231; Schnauss, *Chem. Zeit.*, 1892, 16, 842; Stieglitz, *Phot. Arch.*, 1892, 33, 52; Namias, *Bayerisches Industrie und Gewerbeblatt*, 1895, 26, 529; Lumière and Seyewitz, *Mon. scient.*, 1905, [4], 19, 101.

<sup>4</sup> Kužel, *German Patents*, 194348, 194707 (1905); Planchon, *German Patent*, 194896 (1907).

<sup>5</sup> Giolitti and Agamennone, *Atti R. Accad. Lincei*, 1905, [5], 14, i, 114, 165.

<sup>6</sup> Smithells, *Trans. Chem. Soc.*, 1883, 43, 125; Giolitti and Agamennone, *loc. cit.* Cf. Ditte, *Compt. rend.*, 1880, 91, 115. See also Bolton, *Bull. Soc. chim.*, 1866, 2, 450; *Ber. Preuss. Akad.*, 1866, p. 299; *On the Fluorine Compounds of Uranium*, Berlin, 1866, p. 15.

<sup>7</sup> Hermann, *Über einige Uranverbindungen*, Göttingen, 1861, p. 32.

<sup>8</sup> Bolton, *Jahresber.*, 1886, p. 209.

<sup>9</sup> Ruff and Heinzelmann, *Zeitsch. anorg. Chem.*, 1911, 72, 63.

<sup>10</sup> Giolitti, *Gazzetta*, 1904, 34, ii, 166.

voluminous green precipitate produced by adding hydrofluoric acid to a solution of uranous chloride.

*Double fluorides* have been obtained by reduction of complex alkali uranyl fluoride solutions by means of oxalic or formic acid under the influence of sunlight.<sup>1</sup> The potassium salt,  $\text{KUF}_5$ , is a green powder, insoluble in water.

**Uranous Oxyfluoride**,  $\text{UOF}_2$ , is formed as a fine green precipitate when hydrofluoric acid acts on urano-uranic oxide.<sup>2</sup> A solution of uranyl formate in formic acid, partly reduced by exposure to sunlight, yields, on addition of hydrofluoric acid, a precipitate of composition  $\text{UOF}_2 \cdot 2\text{H}_2\text{O}$ . A green double salt, of composition  $\text{UOF}_2 \cdot \text{NH}_4\text{F}$ , is obtained by electrolysing a solution of uranyl ammonium carbonate containing excess of hydrofluoric acid.

When uranous fluoride is dissolved in a solution of ammonium oxalate a dark green liquid results, which exhibits a violet fluorescence and deposits on evaporation crystals of the double salt  $\text{UF}_4 \cdot 2(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ .<sup>3</sup>

**Uranium Hexafluoride**, **Uranic Fluoride**,  $\text{UF}_6$ , is the only known compound of hexavalent uranium (with the possible exception of the boride in which the condition of the uranium is not established) which does not contain oxygen. It was first prepared by Ruff and Heinzelmann<sup>4</sup> by the action of fluorine on uranium pentachloride at  $-40^\circ \text{C}$ . The action proceeds as already described (see equation above), and the volatile hexafluoride is distilled off from the tetrafluoride. The pentachloride, when acted upon by dry hydrogen fluoride, yields a compound,  $\text{UF}_5 \cdot x\text{HF}$ , which breaks up on distillation into the tetra- and hexafluorides, but this method of preparation is less convenient than the preceding one owing to the difficulty of separating the hexafluoride from hydrogen fluoride. Uranium carbide reacts with fluorine in presence of a little chlorine at  $-70^\circ \text{C}$ ., with formation of the hexafluoride.

Uranium hexafluoride yields glistening, colourless or pale yellow, monoclinic crystals,<sup>5</sup> which fume in the air and sublime under reduced pressure at ordinary temperature. It boils at  $56.2^\circ \text{C}$ ., and the calculated mean latent heat of evaporation between  $42^\circ$  and  $57^\circ \text{C}$ . is 29.4 calories per gram (=10360 calories per gram molecule). The variation of the boiling-point with the vapour pressure is as follows :

Temperature, $^\circ \text{C}$ . . . . .	56.2	48	45	41	37
Pressure, mm. . . . .	764.6	521.2	410.1	406.1	298.2

The crystals melt at  $69.2^\circ \text{C}$ . at which temperature the vapour pressure is (by extrapolation) 1490 mm. or about 2 atmospheres.<sup>6</sup> The vapour density at  $448^\circ \text{C}$ . is 11.7 (air=1), corresponding to a molecular weight of 338 (the theoretical value being 12.16).

The crystals have density at  $20.7^\circ \text{C}$ ., 4.68. They are very hygroscopic and soluble in water. Chemically, uranium hexafluoride is highly reactive, vigorously attacking alcohol, ether, or benzene, in the

<sup>1</sup> Bolton, *Ber. Preuss. Akad.*, 1866, p. 299.

<sup>2</sup> Giolitti and Agamennone, *Atti R. Accad. Lincei*, 1905, [5], 14, i., 114, 165.

<sup>3</sup> Orloff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 1247.

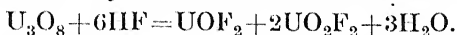
<sup>4</sup> Ruff and Heinzelmann, *Zeitsch. anorg. Chem.*, 1911, 72, 63.

<sup>5</sup> Ruff, Zedner, Schiller, and Heinzelmann, *Ber.*, 1909, 42, 492; Ruff and Heinzelmann, *loc. cit.*

<sup>6</sup> Compare the behaviour of solid carbon dioxide, this series, Vol. V., p. 121.

last case depositing carbon. It reacts more slowly with carbon disulphide, paraffin, chloroform, and nitrobenzene. It dissolves readily in tetrachlorethane. It attacks glass in presence of a trace of moisture, forming silicic tetrafluoride and uranium oxyfluoride. It is decomposed by nitric acid. Ammonia forms ammonium uranate and fluoride. It is reduced by most non-metals and metals, except gold and platinum. Sulphur forms the disulphide,  $US_2$ , and uranous fluoride, and a gas is evolved which appears to be a new fluoride of sulphur. It is stable in presence of dry air, oxygen, nitrogen, carbon dioxide, chlorine, bromine, or iodine.

**Uranyl Fluoride,  $UO_2F_2$ ,** is formed with uranous oxyfluoride (see above) by the action of hydrofluoric acid on urano-uranic oxide : <sup>1</sup>



The green insoluble uranous oxyfluoride is removed by filtration, and the uranyl fluoride remains as a yellow mass after evaporation of the solution. It is also obtained as a yellow powder by repeated evaporation of uranyl acetate with hydrofluoric acid.<sup>2</sup> A white crystalline form has been described by Smithells,<sup>3</sup> who obtained it by carefully heating the tetrafluoride in air; it dissolved in water yielding a yellow solution.

Complex uranyl fluorides of the type  $UO_2F_2 \cdot 3RF$  ( $R=K, NH_4$ ) have been obtained by the addition of excess of the alkali fluoride to a solution of uranyl fluoride, both the yellow and the white variety acting in this way.<sup>4</sup> A solution of uranyl acetate, or of potassium diuranate containing hydrofluoric acid, with excess of the alkali fluoride, also yields the same compounds. The potassium salt,  $UO_2F_2 \cdot 3KF$ , separates as a heavy orange-yellow crystalline precipitate; it is dimorphous, and the crystals may be tetragonal or monoclinic according to the method of preparation. At 20° C. the crystals have density 4.263. The addition of excess of hydrogen peroxide to a solution of this salt gives a yellow solution from which a yellow peroxyfluoride, of composition  $3(UO_4 \cdot KF) \cdot UO_2F_2 \cdot KF \cdot 4H_2O$ , separates on keeping.<sup>5</sup> The ammonium salt,  $UO_2F_2 \cdot 3NH_4F$ , only yields crystals of the tetragonal form, the density of which at 20° C. is 3.186.

If the potassium salt is dissolved in water containing not more than 13 per cent. of the acid fluoride of potassium, the solution on concentration yields triclinic crystals of the compound  $2UO_2F_2 \cdot 5KF$ .<sup>6</sup> If excess of uranyl nitrate is present in the solution, monoclinic crystals of the compound  $2UO_2F_2 \cdot 3KF$  are obtained.

A soluble uranyl silicofluoride has been described.<sup>7</sup>

#### URANIUM AND CHLORINE.

**Uranium Trichloride,  $UCl_3$ ,** may be obtained <sup>8</sup> by heating uranous chloride in hydrogen. It is a reddish-brown substance which readily

<sup>1</sup> Giolitti and Agamennone, *Atti R. Accad. Lincei*, 1905, [5], 14, i., 114; Smithells, *Trans. Chem. Soc.*, 1883, 43, 125; Bolton, *Bull. Soc. chim.*, 1866, 2, 450. See also Ditte, *Compt. rend.*, 1880, 91, 115.

<sup>2</sup> von Unruh, *Einwirkung von Ammoniak auf Uranylsalze*, Dissertation, Rostock, 1909.

<sup>3</sup> Smithells, *loc. cit.*

<sup>4</sup> Bolton, *loc. cit.*; Baker, *Trans. Chem. Soc.*, 1879, 35, 763; *Annalen*, 1880, 202, 240; Smithells, *loc. cit.*

<sup>5</sup> Lordkipanidzé, *J. Russ. Phys. Chem. Soc.*, 1900, 32, 283.

<sup>6</sup> Smithells, *loc. cit.*; Baker, *loc. cit.*

<sup>7</sup> Stolba, *Zeitsch. anal. Chem.*, 1864, 3, 72.

<sup>8</sup> Péligot, *Ann. Chim. Phys.*, 1842, 5, 20.

dissolves in water, yielding a red solution. It may be crystallised in the form of glistening, dark red, hygroscopic needles. The solution is not stable, but gradually turns green with evolution of hydrogen.

The chloride may also be obtained in solution by the reduction of uranyl salts in hydrochloric acid solution, either by means of nascent hydrogen,<sup>1</sup> or by electrolysis<sup>2</sup> in a special apparatus, in which a layer of mercury is used as the cathode, the anode being of carbon, and the whole is cooled in ice. In the latter case, traces of dissolved mercury or platinum are liable to act as negative catalysts and stop the reduction when the uranium is in the tetravalent condition. The solutions of the trichloride obtained contain excess of hydrochloric acid and are purple red; they are comparatively stable, but are readily converted into uranous compounds.

**Uranium Tetrachloride, Uranous Chloride,  $\text{UCl}_4$ ,** may be prepared by heating uranium, uranium carbide,<sup>3</sup> or a mixture of any oxide of uranium, or uranyl chloride, with carbon,<sup>4</sup> in a stream of chlorine. A small quantity of the pentachloride is also formed, but this may be converted to the tetrachloride by heating at  $235^\circ \text{C}$ . in a current of carbon dioxide.<sup>5</sup> Uranous chloride may also be obtained by

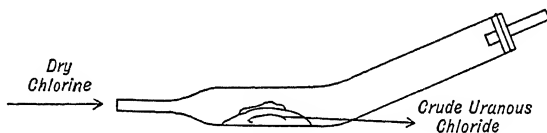


FIG. 6.

the action of gaseous hydrogen chloride on uranous oxide;<sup>6</sup> or by heating urano-uranic oxide in a current of carbon tetrachloride vapour, or in a mixture of chlorine and sulphur chloride.<sup>7</sup> The product can be purified by sublimation in a vacuum, or by heating to redness in an atmosphere of dry chlorine. In the latter case, a hard glass tube, of about 4 cm. diameter (see fig. 6), may be used;<sup>8</sup> the uranous chloride is deposited close to the hot zone in the form of a green crystalline mass. It may be obtained in solution by exposing to the action of sunlight a solution in hydrochloric acid of uranic hydroxide, or of the green hydroxide, in presence of a little alcohol;<sup>9</sup> or by reduction of uranyl chloride by means of copper and hydrochloric acid in presence of traces of platonic chloride;<sup>10</sup> it is obtained as a green crystalline precipitate on adding ether.

<sup>1</sup> Zimmermann, *Annalen*, 1882, 213, 285.

<sup>2</sup> Rosenheim and Loebel, *Zeitsch. anorg. Chem.*, 1908, 57, 234.

<sup>3</sup> Moissan, *Compt. rend.*, 1896, 122, 1088.

<sup>4</sup> Péligot, *Annalen*, 1842, 43, 258; Roscoe, *Trans. Chem. Soc.*, 1874, 27, 933; Ber., 1874, 7, 1131; Zimmermann, *Annalen*, 1882, 213, 320; 1883, 216, 8; Roderburg, *Zeitsch. anorg. Chem.*, 1913, 81, 122.

<sup>5</sup> Roscoe, *loc. cit.*

<sup>6</sup> Rose, *Pogg. Annalen*, 1862, 116, 352.

<sup>7</sup> Colani, *Ann. Chim. Phys.*, 1907, [8], 12, 59; Camboulives, *Compt. rend.*, 1910, 150, 175; Lely, jun., and Hamburger, *Zeitsch. anorg. Chem.*, 1914, 87, 209; Moore, *J. Amer. Electrochem. Soc.*, 1923, 43, 317.

<sup>8</sup> Moore, *loc. cit.*

<sup>9</sup> Aloy, *Ann. Chim. Phys.*, 1901, [7], 24, 412; *Bull. Soc. chim.*, 1899, [3], 21, 613.

<sup>10</sup> Arendt and Knop, *Chem. Zentr.*, 1857, p. 164. See also Kohlschütter and Rossi, *Ber.*, 1901, 34, 1472.

Uranous chloride yields lustrous, dark green, octahedral crystals which sublime when heated to redness. The vapour density is 13.33 (air=1),<sup>1</sup> corresponding to molecular weight 386.0 ( $\text{UCl}_4=380.0$ ). By ebullioscopic determinations of the molecular weight, using molten bismuth chloride as solvent, Rügheimer and Gonder<sup>2</sup> obtained the value 373. The crystals fume in the air and are very deliquescent. They readily dissolve in water, with evolution of heat, yielding a green solution which is fairly stable in the cold, but is hydrolysed to a considerable extent and gives an acid reaction. It is a powerful reducing agent, and on evaporation, hydrochloric acid fumes escape, and on prolonged heating or boiling, a black precipitate is produced which appears to be an oxychloride of composition  $\text{UCl}_4 \cdot 5\text{UO}_2 \cdot 10\text{H}_2\text{O}$ .<sup>3</sup> On complete evaporation an amorphous deliquescent mass is obtained which when heated leaves urano-uranic oxide. Uranous chloride dissolves readily in ethyl alcohol, acetone, and other organic solvents.<sup>4</sup>

It is reduced to the metal by the action of alkali metals (see p. 279). Heated in hydrogen, it yields the trichloride; in ammonia, a nitride;<sup>5</sup> in hydrogen sulphide, a sulphide.<sup>6</sup>

The **oxychloride**,  $\text{UCl}_4 \cdot 2\text{UO}_2 \cdot 13\text{H}_2\text{O}$ , may be obtained<sup>7</sup> as green crystals by the action of light on a solution of uranyl chloride in a mixture of alcohol and ether. When dried over sulphuric acid the salt loses water and leaves the monohydrate,  $\text{UCl}_4 \cdot 2\text{UO}_2 \cdot \text{H}_2\text{O}$ . This on heating at  $100^\circ \text{C}$ . becomes brownish-black and yields  $\text{UCl}_4 \cdot 4\text{UO}_2$ . Both hydrates dissolve in water and alcohol, forming green solutions.

**Double Chlorides** of the type  $\text{R}_2\text{UCl}_6$  ( $\text{R}=\text{Na}, \text{K}, \text{Li}$ ;  $\text{R}_2=\text{Ca}, \text{Sr}, \text{Ba}$ ) have been obtained<sup>8</sup> by passing uranous chloride vapour over the chloride of the alkali or alkaline earth metal heated to dull redness. The salts, which are green, are hygroscopic, and darken as they absorb moisture from the air. They are unstable, and their solutions oxidise slowly at ordinary temperature and more rapidly when heated. When evaporated in a vacuum over sulphuric acid they decompose, so that the salts cannot be obtained in the crystalline form.

The double salt, **uranous chlorophosphate**,  $\text{UCl}_4 \cdot \text{UH}_2(\text{PO}_4)_2$ , separates in green crystals from a solution of uranous phosphate,  $\text{UH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ , in concentrated hydrochloric acid.<sup>9</sup> A chlorophosphate, of composition  $\text{UCl}_4 \cdot 3\text{UO}_2 \cdot 2\text{P}_2\text{O}_5$ , has also been prepared (see p. 328).

**Uranium Pentachloride**,  $\text{UCl}_5$ , is formed in small quantity during the preparation of uranous chloride by chlorination of uranium or its oxides, either by heating in a stream of chlorine or of carbon tetrachloride vapour<sup>10</sup> (see p. 294); it forms as a sublimate further from the heated material than the tetrachloride. It exists in two forms:<sup>11</sup>

<sup>1</sup> Zimmermann, *Annalen*, 1882, 216, 8.

<sup>2</sup> Rügheimer and Gonder, *ibid.*, 1908, 364, 45.

<sup>3</sup> Aloy, *Bull. Soc. chim.*, 1899, [3], 21, 613.

<sup>4</sup> Merton, *Trans. Chem. Soc.*, 1914, 105, 23.

<sup>5</sup> Uhrlaub, *Verbindungen einiger Metalle mit Stickstoff*, Göttingen, 1859, p. 27.

<sup>6</sup> Hermann, *Uranverbindungen*, Göttingen, 1861, p. 60.

<sup>7</sup> Orloff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 513. See also *ibid.*, 1902, 34, 375.

<sup>8</sup> Moissan, *Compt. rend.*, 1896, 122, 1088; Aloy, *Bull. Soc. chim.*, 1899, [3], 21, 264.

<sup>9</sup> Aloy, *Ann. Chim. Phys.*, 1901, [7], 24, 412.

<sup>10</sup> Roscoe, *loc. cit.*; Michael and Murphy, *Amer. Chem. J.*, 1910, 44, 365; Camboulives, *Compt. rend.*, 1910, 150, 175; Bourion, *Ann. Chim. Phys.*, 1910, [8], 21, 58.

<sup>11</sup> Roscoe, *loc. cit.*

long lustrous needle-shaped crystals, dark green by reflected, but ruby red by transmitted, light, and a light brown mobile powder. Both forms are very hygroscopic and are decomposed by water. The pentachloride cannot be volatilised without decomposition, for on heating it dissociates into uranous chloride and chlorine. In an atmosphere of carbon dioxide the dissociation is complete at 235° C.

**Uranyl Chloride,  $\text{UO}_2\text{Cl}_2$ ,** is obtained in the anhydrous condition by the action of chlorine on heated uranous oxide.<sup>1</sup> It yields a yellow crystalline mass, stable in dry air but very hygroscopic and readily soluble in water. It is also soluble in alcohol or ether. When heated in air, uranyl chloride loses chlorine and leaves uranous oxide which is oxidised to higher oxides. If heated to redness in hydrogen, it is reduced to uranous oxide.<sup>2</sup> Fusion with excess of caustic potash in an open tube produces a red peruranate,  $\text{K}_2\text{UO}_5$ , which gradually changes to the yellow uranate,  $\text{K}_2\text{UO}_4$ , with loss of oxygen.

It is formed in solution by oxidising uranous chloride with nitric acid; by dissolving uranic oxide in concentrated hydrochloric acid;<sup>3</sup> or by adding barium chloride to a concentrated solution of uranyl sulphate until precipitation is complete.<sup>4</sup> Its aqueous solution on evaporation yields the monohydrate,  $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ .<sup>5</sup> The solution is unstable at ordinary temperatures and slowly deposits uranic hydroxide, which after a time partly redissolves. The uranyl chloride may be reduced in solution to black uranous oxide by the action of magnesium or aluminium powder.<sup>6</sup> The densities of aqueous solutions of uranyl chloride have been determined as follows:<sup>7</sup>

Temperature, ° C.	Concentration, $\text{UO}_2\text{Cl}_2$ per cent.	Density.
14.6	1	1.0056
16.3	2	1.0112
13.7	3	1.0161
13.1	4	1.0215
14.2	5	1.0260
15.2	6	1.0313
14.3	7	1.0366
14.5	8	1.0418
15.0	9	1.0469
14.8	10	1.0517

The equivalent conductivities of aqueous solutions containing  $\frac{1}{2}\text{UO}_2\text{Cl}_2$  in  $v$  litres at 25° C. are as follows:<sup>8</sup>

$v =$	4	8	16	32	64	128	256	512	1024
$\Lambda =$	79.8	89.3	96.6	104.3	111.3	118.5	127.4	136.4	147.0

<sup>1</sup> Péligot, *Ann. Chim. Phys.*, 1842, [3], 5, 5.

<sup>2</sup> O. de Coninck, *Compt. rend.*, 1908, 147, 1477.

<sup>3</sup> Mylius and Dietz, *Ber.*, 1901, 34, 2774.

<sup>4</sup> O. de Coninck, *Compt. rend.*, 1909, 148, 1769; *Bull. Acad. roy. Belg.*, 1909, p. 836;

*Ann. Chim. Phys.*, 1904, [8], 3, 500.

<sup>5</sup> O. de Coninck, *loc. cit.*; cf. Mylius and Dietz, *loc. cit.*

<sup>6</sup> O. de Coninck, *Bull. Acad. roy. Belg.*, 1909, p. 744.

<sup>7</sup> O. de Coninck, *Ann. Chim. Phys.*, 1904, [8], 3, 500.

<sup>8</sup> Dittrich, *Zeitsch. physikal. Chem.*, 1899, 29, 449. For conductivities at 35°, 50°, and 65° C., see West and Jones, *Amer. Chem. J.*, 1910, 44, 508.

From the solution in hydrochloric acid, the *trihydrate*,  $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ , possibly  $\text{H}_4\text{UO}_5 \cdot 2\text{HCl}$ , separates<sup>1</sup> in yellowish-green hygroscopic prisms, which when heated above  $100^\circ \text{C}$ . decompose, losing water, hydrogen chloride, and chlorine. The trihydrate dissolves in water, 1 part in 0.134 part of water at  $18^\circ \text{C}$ ., yielding a viscous solution of density 2.74.

A saturated solution of uranyl chloride in hydrochloric acid when cooled to  $-10^\circ \text{C}$ . yields yellow crystals of an unstable hydrochloride,  $\text{UO}_2\text{Cl}_2 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ .<sup>2</sup> The compound may also be obtained by the action of hydrochloric acid on uranyl nitrate.<sup>3</sup>

Compounds of uranyl chloride with ammonia, of composition  $\text{UO}_2\text{Cl}_2 \cdot 2\text{NH}_3$  and  $\text{UO}_2\text{Cl}_2 \cdot 3\text{NH}_3$ , and with organic compounds, for example  $\text{UO}_2\text{Cl}_2 \cdot 2\text{NH}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  and  $\text{UO}_2\text{Cl}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ , have been described.<sup>4</sup> Well crystallised compounds with organic bases have also been prepared.<sup>5</sup>

Uranyl chloride reacts with the chlorides of the alkali metals to form a series of complex salts of the type  $\text{R}_2(\text{UO}_2)\text{Cl}_4$ . Uranyl potassium chloride,  $\text{K}_2(\text{UO}_2)\text{Cl}_4$ , is prepared in the anhydrous condition by passing dry chlorine first over heated uranous oxide and then over heated potassium chloride.<sup>2</sup> It is obtained as a golden-yellow powder which when heated to redness melts without decomposition. It is very soluble in water. The *dihydrate*,  $\text{K}_2(\text{UO}_2)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , separates on evaporation of a solution containing potassium chloride and uranyl chloride;<sup>6</sup> or of a hydrochloric acid solution of potassium uranate.<sup>7</sup> It yields greenish-yellow, triclinic pinacoidal plates.<sup>8</sup> The double salt can only be obtained pure from the aqueous solution above  $60^\circ \text{C}$ ., as below this temperature it undergoes partial decomposition with separation of potassium chloride.<sup>9</sup> The ammonium salt,  $(\text{NH}_4)_2(\text{UO}_2)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , prepared by crystallisation from a solution of ammonium and uranyl chlorides in concentrated hydrochloric acid, is isomorphous with the potassium salt,<sup>10</sup> and behaves similarly with water.<sup>9</sup> The sodium salt,  $\text{Na}_2(\text{UO}_2)\text{Cl}_4$ , obtained in the dry way by passing chlorine successively over heated uranous oxide and sodium chloride,<sup>2</sup> is a golden-yellow substance with properties similar to the anhydrous potassium salt. The rubidium salt,  $\text{Rb}_2(\text{UO}_2)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , is isomorphous with the potassium and ammonium salts, but differs from them in being undecomposed by water both at high and low temperatures. The caesium compound,  $\text{Cs}_2(\text{UO}_2)\text{Cl}_4$ , is obtained in yellow rhombic leaflets from an aqueous solution of the mixed chlorides containing hydrochloric acid.<sup>11</sup> Like the rubidium salt, it is stable towards water.

<sup>1</sup> Mylius and Dietz, *loc. cit.*

<sup>2</sup> Aloy, *Bull. Soc. chim.*, 1901, [3], 25, 153.

<sup>3</sup> O. de Coninck, *Recherches sur le nitrate d'uranium*, Montpellier, 1901.

<sup>4</sup> Regelsberger, *Annalen*, 1885, 227, 119; see also Ordway, *Amer. J. Sci.*, 1858, [2], 26, 208; *Jahresber.*, 1858, p. 115; von Unruh, *Einwirkung von Ammoniak auf Uranylsalze*, Dissertation, Rostock, 1909.

<sup>5</sup> Rimbach, *Ber.*, 1904, 37, 461; Grossmann and Schück, *Zeitsch. anorg. Chem.*, 1906, 50, 21; see also Williams, *J. prakt. Chem.*, 1856, 69, 355.

<sup>6</sup> Arfvedson, *Pogg. Annalen*, 1824, 1, 245; *Schweigger's J.*, 1825, 44, 8; Berzelius, *Pogg. Annalen*, 1824, 1, 359; *Schweigger's J.*, 1825, 44, 191.

<sup>7</sup> Péligot, *loc. cit.*

<sup>8</sup> Rammelsberg, *Handb. d. kristallogr. Chemie*, Berlin, 1855, p. 215; de la Provostaye, *Ann. Chim. Phys.*, 1842, [3], 6, 165.

<sup>10</sup> Groth, *Chemische Kristallographie*, 1908, i., 595.

<sup>11</sup> Wells and Boltwood, *Zeitsch. anorg. Chem.*, 1895, 10, 181.

<sup>9</sup> Rimbach, *loc. cit.*



**Uranyl Chlorate**,  $\text{UO}_2(\text{ClO}_3)_2 \cdot x\text{H}_2\text{O}$ , is obtained by the addition of barium chlorate to a solution of uranyl sulphate.<sup>1</sup> After filtration and evaporation, crystals are obtained which are readily soluble in water.

**Uranyl Perchlorate**,  $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , is prepared by adding perchloric acid to a solution of potassium uranate, filtering off the precipitated potassium perchlorate, and evaporating the filtrate over phosphorus pentoxide.<sup>2</sup> It forms yellow prismatic crystals, which melt at  $90^\circ \text{C.}$ , and at  $100^\circ \text{C.}$  lose water, yielding the *tetrahydrate*,  $\text{UO}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ .

#### URANIUM AND BROMINE.

**Uranium Tribromide**,  $\text{UBr}_3$ , is obtained by reduction of uranous bromide in a stream of hydrogen.<sup>3</sup> It yields dark brown needles with properties similar to those of the trichloride (see p. 293).

**Uranium Tetrabromide, Uranous Bromide**,  $\text{UBr}_4$ , is prepared by passing a mixture of nitrogen or carbon dioxide and bromine vapour over a heated mixture of urano-uranic oxide and charcoal.<sup>4</sup> The product may be purified by sublimation in absence of air (see p. 284). It may also be prepared by heating fused uranous chloride in a current of hydrogen bromide.<sup>5</sup> The bromide is deposited as a sublimate consisting of lustrous dark brown leaflets, of density 4.838 at  $21^\circ \text{C.}$  At red heat it yields a dark brown vapour of density 19.46 (air=1),<sup>7</sup> corresponding to a molecular weight 536.6. The theoretical value for  $\text{UBr}_4$  is 557.9. Uranous bromide is hygroscopic and very soluble in water, but the solution resembles that of uranous chloride in being unstable; hydrogen bromide escapes, and by oxidation yellow uranyl bromide is formed.

*Double bromides* of the type  $\text{R}_2\text{UBr}_6$ , similar to the corresponding chlorides, have been prepared by passing uranium tetrabromide vapour over the heated alkali bromides.<sup>8</sup> The potassium and sodium salts,  $\text{K}_2\text{UBr}_6$  and  $\text{Na}_2\text{UBr}_6$ , are green crystalline substances, hygroscopic, but less so than uranium tetrabromide.

**Uranyl Bromide**,  $\text{UO}_2\text{Br}_2$ .—When uranous oxide is heated in a current of bromine vapour a mixture of uranyl bromide and uranous bromide is formed. The former can be extracted with ether, and obtained as yellowish-green fluorescent needles by evaporation of the solution. It is obtained in aqueous solution by the action of bromine water on uranous oxide, or of hydrobromic acid on uranic oxide;<sup>9</sup> yellow needles of the heptahydrate,  $\text{UO}_2\text{Br}_2 \cdot 7\text{H}_2\text{O}$ , separate on concentrating the solution. Uranyl bromide is very deliquescent and is decomposed in moist air to hydrated uranic oxide and hydrobromic

<sup>1</sup> Rammelsberg, *Pogg. Annalen*, 1842, 55, 77.

<sup>2</sup> Salvadori, *Chem. Zeit.*, 1912, 36, 513.

<sup>3</sup> Alibegoff, *Annalen*, 1886, 233, 117.

<sup>4</sup> Zimmermann, *Ber.*, 1882, 15, 847; *Annalen*, 1883, 216, 1; Hermann, *Über einige Uranverbindungen*, Göttingen, 1861, p. 32; Colani, *Compt. rend.*, 1903, 137, 382; Richards and Merigold, *Chem. News*, 1902, 85, 177; *Zeitsch. anorg. Chem.*, 1902, 31, 235; *Proc. Amer. Acad.*, 1902, 37, 365.

<sup>5</sup> Colani, *Ann. Chim. Phys.*, 1907, [8], 12, 59.

<sup>6</sup> Richards and Merigold, *loc. cit.*

<sup>7</sup> Zimmermann, *loc. cit.*

<sup>8</sup> Moissan, *Compt. rend.*, 1896, 122, 1089; *Bull. Soc. chim.*, 1897, [3], 17, 267; Aloy, *ibid.*, 1899, [3], 21, 264.

<sup>9</sup> Sendtner, *Annalen*, 1875, 195, 325.

acid ; <sup>1</sup> in dry air it gradually evolves bromine. The solution in water decomposes on keeping, and deposits the yellow hydrate of uranic oxide. When heated, it evolves bromine and hydrogen bromide, and leaves a brick-red residue of uranous oxide.<sup>2</sup>

The *double chlorides*,  $K_2(UO_2)Br_4 \cdot 2H_2O$  and  $(NH_4)_2(UO_2)Br_4 \cdot 2H_2O$ , have been prepared<sup>3</sup> by acting upon solutions of the alkali uranates with hydrobromic acid. They are separated as yellowish-brown crystals.

Uranyl bromate does not appear to be stable. If a solution of uranyl sulphate is treated with barium bromate, and the filtrate after removal of the precipitate is subjected to evaporation, bromine escapes and a syrupy liquid remains which appears to be a basic bromate.<sup>4</sup>

### URANIUM AND IODINE.

**Uranium Tetra-iodide, Uranous Iodide,  $UI_4$** , is obtained by passing iodine vapour over powdered uranium heated to  $500^\circ C$ . in a vacuum tube.<sup>5</sup> It forms as a sublimate consisting of fine black needle-shaped crystals, of density 5.6 at  $15^\circ C$ . On heating, it melts at about  $500^\circ C$ ., and in air readily oxidises to urano-uranic oxide. It is reduced when heated in hydrogen. It is soluble in water, yielding a green acid solution which gives the characteristic reactions of uranous salts and, like the solutions of the corresponding chloride and bromide, is unstable.

**Uranyl Iodide,  $UO_2I_2$** , is prepared by adding barium iodide in slight excess to an ethereal solution of uranyl nitrate.<sup>6</sup> It separates in red crystals which are deliquescent and unstable, losing iodine in the air, and in aqueous solution forming hydriodic acid and free iodine.<sup>7</sup>

**Uranyl Iodate,  $UO_2(IO_3)_2$** , is obtained by precipitation of a solution of uranyl nitrate by means of sodium iodate in presence of a large excess of nitric acid. According to Ditte,<sup>8</sup> the anhydrous salt is obtained as yellow crystals by mixing the boiling solutions and crystallising at  $60^\circ C$ . A *pentahydrate*,  $UO_2(IO_3)_2 \cdot 5H_2O$ , is obtained when iodic acid or sodium iodate is added to a cold solution of uranyl acetate. When heated to  $250^\circ C$ . the iodate decomposes, yielding iodine and urano-uranic oxide. According to Artmann,<sup>9</sup> however, the iodate does not exist in the anhydrous condition, but only as the mono- and di-hydrates, the nature of the product in the precipitation of uranyl nitrate by means of sodium iodate depending upon the conditions. From hot and acid solutions the *monohydrate*,  $UO_2(IO_3)_2 \cdot H_2O$ , is obtained, while from cold solutions the *dihydrate*,  $UO_2(IO_3)_2 \cdot 2H_2O$ , is precipitated. The monohydrate exists in two modifications : a rhombic prismatic form, stable at ordinary temperatures, of density 5.220 at  $18^\circ C$ ., and a pyramidal form of density 5.052 at  $18^\circ C$ . The former is converted into the latter by boiling with water, while the reverse change takes place slowly at ordinary temperatures. The two varieties differ

<sup>1</sup> O. de Coninck, *Bull. Acad. roy. Belg.*, 1902, **12**, 1025.

<sup>2</sup> O. de Coninck, *Compt. rend.*, 1902, **135**, 900.

<sup>3</sup> Sendtner, *loc. cit.*

<sup>4</sup> Rammelsberg, *loc. cit.*

<sup>5</sup> Guichard, *Compt. rend.*, 1907, **145**, 921. See also Moissan, *ibid.*, 1896, **122**, 274.

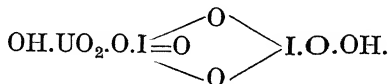
<sup>6</sup> Aloy, *Ann. Chim. Phys.*, 1901, [7], **24**, 412.

<sup>7</sup> Aloy, *loc. cit.* ; *Recherches sur l'uranium et ses composés*, Thèse 21, Paris, 1901, p. 14 ; von Unruh, *Dissertation*, Rostock, 1909.

<sup>8</sup> Ditte, *Thèse*, Paris, 1870.

<sup>9</sup> Artmann, *Zeitsch. anorg. Chem.*, 1913, **79**, 327 ; 1913, **80**, 280.

in solubility, 100 c.c. of water dissolving at 18° C. 0.1049 gram of the prismatic form and 0.1214 gram of the pyramidal form. The dihydrate has a lighter yellow colour and crystallises in irregular aggregates. It is slightly soluble in water, the solution being strongly acid. When heated, uranyl iodate retains one molecule of water and does not become anhydrous. Artmann, therefore, suggests that the molecule of the compound should be represented by the formula  $(\text{OH})(\text{UO}_2)\text{IO}_3 \cdot \text{H}_2\text{O}$ , *i.e.*



The potassium salt,  $\text{K}(\text{UO}_2)(\text{IO}_3)_3 \cdot 3\text{H}_2\text{O}$ , is precipitated when potassium iodate is added in large excess to uranyl iodate solution as a light yellow powder of density 3.706. It is sparingly soluble in and is hydrolysed by water; it is converted into uranyl iodate by excess of uranyl nitrate.

#### URANIUM AND OXYGEN.

The two chief oxides of uranium are the basic uranous oxide  $\text{UO}_2$  and the acid anhydride  $\text{UO}_3$ . Intermediate between these two is a well-defined green oxide of composition  $\text{U}_3\text{O}_8$ . Less certain<sup>1</sup> is the existence of a pentoxide  $\text{U}_2\text{O}_5$ , and a tetroxide, uranium peroxide,  $\text{UO}_4$ , though well-defined derivatives of the latter, peruranates, are known.

**Uranous Oxide, Uranium Dioxide,  $\text{UO}_2$ ,** owing to its stability and metallic appearance, was until 1842 thought to be the element. It may be obtained as a brown amorphous powder, usually pyrophoric, by reducing the green oxide,  $\text{U}_3\text{O}_8$ ,<sup>2</sup> or uranyl oxalate,<sup>3</sup> by heating in a current of hydrogen; by igniting the higher oxides in an indifferent atmosphere, such as carbon dioxide or nitrogen;<sup>4</sup> or by heating urano-uranic oxide with ammonium chloride,<sup>5</sup> ammonium chloride and sulphur,<sup>6</sup> or anhydrous oxalic acid. It is also produced by reducing uranyl sulphate or nitrate<sup>7</sup> in hydrogen; or by heating together uranyl phosphate, potassium carbonate, and potassium cyanide;<sup>8</sup> or by electrolysis of a solution of uranyl nitrate.<sup>9</sup> It is obtained as a black powder by reducing an aqueous solution of uranyl chloride by means of powdered aluminium or magnesium.<sup>10</sup>

Uranous oxide is also obtained in the form of black microscopic crystals when urano-uranic oxide is reduced with carbon or heated with a little hydrofluoric acid;<sup>11</sup> when crystallised uranic hydroxide is heated in hydrogen;<sup>12</sup> when uranyl chloride is heated with potassium in a current of hydrogen,<sup>13</sup> or with a mixture of ammonium and sodium

<sup>1</sup> Lebeau, *Compt. rend.*, 1922, 174, 388; Jolibois and Bossuet, *ibid.*, 1922, 174, 386.

<sup>2</sup> Arfvedson, *Pogg. Annalen*, 1823, 1, 128.

<sup>3</sup> Péligot, *Ann. Chim. Phys.*, 1842, [3], 5, 5; Ebelmen, *ibid.*, 1842, [3], 5, 189; Raynaud, *Bull. Soc. chim.*, 1912, [4], 11, 802; *Compt. rend.*, 1912, 154, 1480.

<sup>4</sup> Zimmermann, *Annalen*, 1886, 232, 273. See also Colani, *Compt. rend.*, 1903, 137, 382; *Ann. Chim. Phys.*, 1907, [8], 12, 59; Mixer, *Zeitsch. anorg. Chem.*, 1912, 78, 221.

<sup>5</sup> Smith and Matthews, *J. Amer. Chem. Soc.*, 1895, 17, 687.

<sup>6</sup> Hermann, *Uranverbindungen*, Göttingen, 1861, p. 17; *Jahresber.*, 1861, p. 258.

<sup>7</sup> Lebeau, *Compt. rend.*, 1912, 155, 163.

<sup>8</sup> Rose, *Traité de chimie analytique*, Paris, 1862, 2, 728.

<sup>9</sup> O. de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, p. 321.

<sup>10</sup> O. de Coninck, *ibid.*, 1909, p. 744.

<sup>11</sup> Ditte, *Compt. rend.*, 1880, 91, 115; *Ann. Chim. Phys.*, 1884, [6], 1, 338.

<sup>12</sup> Aloy, *Bull. Soc. chim.*, 1900, [3], 23, 368.

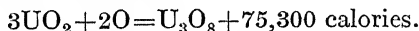
<sup>13</sup> Arfvedson, *loc. cit.*

chlorides ;<sup>1</sup> or when the double chloride,  $\text{Na}_2\text{UCl}_6$ , is heated to redness in a moisture-laden stream of carbon dioxide.<sup>2</sup> Especially fine black cubic crystals are obtained by fusing together 1 part of sodium diuranate and 4 parts of magnesium chloride.<sup>3</sup> The amorphous form may be readily converted into the crystalline variety by fusion with borax, the product being washed with dilute hydrochloric acid, when jet-black octahedra are obtained.<sup>4</sup>

A brick-red variety of uranous oxide has been obtained<sup>5</sup> by calcining uranyl bromide in the air. It is very stable at high temperatures, and is converted to the black modification by heating in hydrogen without any appreciable loss of oxygen.

On a commercial scale uranous oxide is prepared<sup>6</sup> by fusing at red heat a mixture of 35 parts of common salt and 20 parts of sodium uranate with 1 part of powdered charcoal, the heating being continued until the escape of gas ceases. After cooling, the mass is lixiviated with water, and the residue of uranous oxide is washed by decantation. By washing with 5 per cent. hydrochloric acid, any iron, aluminium, or vanadium compounds may be removed, and a commercial product of purity equivalent to 97 per cent.  $\text{U}_3\text{O}_8$  is obtained. If the uranous oxide is required for the production of ferro-uranium, the complete removal of iron is not necessary.

Uranous oxide exists in various forms, depending, as indicated above, on the mode of formation. The crystals are usually regular in form, of density 10.95 to 11.0 at 4° C., and are isomorphous with those of cerium and thorium dioxides.<sup>7</sup> The specific heat, according to Regnault, is 0.0619. The magnetisability of uranous oxide is greater than that of the metal or of the higher oxides, the magnetic susceptibility<sup>8</sup> being  $+7.51 \times 10^{-6}$ . When heated in an atmosphere of nitrogen, the oxide melts at 2176° C.<sup>9</sup> It is the most stable of the oxides of uranium at high temperatures, and in many respects behaves like an element. It cannot be reduced by heating in a current of hydrogen, but it is reduced by carbon at about 1500° C.<sup>10</sup> It combines directly with chlorine and bromine at red heat, uranyl compounds being produced. When heated in oxygen, it is readily oxidised, the action commencing at about 185° C.,<sup>11</sup> and the only product is urano-uranic oxide.<sup>12</sup> The heat of the reaction is as follows :<sup>13</sup>



<sup>1</sup> Wöhler, *Annalen*, 1842, 41, 345; see also Hillebrand, *Zeitsch. anorg. Chem.*, 1893, 3, 243.

<sup>2</sup> Colani, *Compt. rend.*, 1903, 137, 382; *Ann. Chim. Phys.*, 1907, [8], 12, 59.

<sup>3</sup> Hofmann and Höschele, *Ber.*, 1915, 48, 20.

<sup>4</sup> Hillebrand, *loc. cit.*

<sup>5</sup> O. de Coninck, *Compt. rend.*, 1902, 135, 900.

<sup>6</sup> Parsons, *J. Ind. Eng. Chem.*, 1917, 9, 466.

<sup>7</sup> Goldschmidt and Thomassen, *Videnskapsselskapets Skrifter. Mat. Naturv. Klasse*, 1923, p. 5; *Chem. Zentr.*, 1923, i., 1149; Hillebrand, *Zeitsch. anorg. Chem.*, 1893, 3, 243; *Bull. U.S. Geol. Survey*, 1893, p. 113; Hofmann and Höschele, *loc. cit.* Compare Aloy, *loc. cit.*, who obtained orthorhombic crystals. Ebelmen, *loc. cit.*, gives density 10.15 for a red variety obtained by reduction of uranyl oxalate in hydrogen. Compare Raynaud, *loc. cit.*

<sup>8</sup> Wedekind and Horst, *Ber.*, 1915, 48, 105.

<sup>9</sup> Ruff and Goecke, *Zeitsch. angew. Chem.*, 1911, 24, ii., 1459.

<sup>10</sup> Greenwood, *Trans. Chem. Soc.*, 1908, 93, 1483.

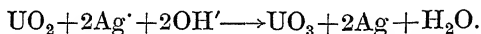
<sup>11</sup> Jolibois and Bossuet, *Compt. rend.*, 1922, 174, 386.

<sup>12</sup> Compare O. de Coninck and Raynaud, *Bull. Soc. chim.*, 1912, [4], 11, 1037.

<sup>13</sup> Mixter, *Amer. J. Sci.*, 1912, [4], 34, 141.

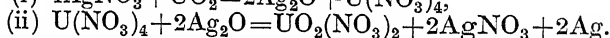
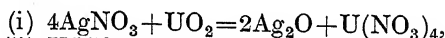
Uranous oxide is only difficultly soluble in hydrochloric and sulphuric acids, even when concentrated. With the latter acid, insoluble uranium sulphate is formed.<sup>1</sup> It readily dissolves, however, in dilute nitric acid forming uranyl nitrate; <sup>2</sup> it is also soluble in aqua regia. The amounts of the oxide dissolving in these acids in a given time vary widely with the mode of preparation of the oxide.

It resembles the dioxide of molybdenum (see p. 131) in being able to reduce salts of silver in ammoniacal solution, with precipitation of silver, thus: <sup>3</sup>



**Colloidal Uranous Oxide.**—During the electrolysis of a solution of uranyl chloride a black reduction product is precipitated at the cathode. This precipitate dissolves in water, forming a dark-coloured colloidal solution, which by titration with potassium permanganate, before and after reduction with zinc, has been shown to contain uranous oxide.<sup>4</sup> A similar solution may be obtained by the reduction of uranyl chloride by zinc or copper in dilute acid solution. When very dilute, the solution has a yellow tinge. In an electric field it becomes decolorised at the anode and precipitation takes place at the cathode. It behaves as a typical positive colloid with coagulating agents.

**Uranous Hydroxide.**—The addition of alkali to a solution of a uranous salt produces a reddish-brown gelatinous precipitate, which darkens in colour on boiling the solution. If dried *in vacuo* it becomes black and has the composition  $\text{UO}_2 \cdot \text{H}_2\text{O}$ . This rapidly oxidises in the air and readily dissolves in dilute acids, forming uranous salts. It acts upon a neutral solution of silver nitrate, first precipitating silver oxide and forming a green solution which, however, soon turns yellow, and the oxide is reduced to metallic silver as the uranyl salt forms in solution,<sup>5</sup> thus:



According to Aloy,<sup>6</sup> a black crystalline hydrate, of composition  $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , is obtained when crystallised uranous sulphate is treated with hot potassium or sodium hydroxide solution. The product, when thoroughly washed, remains stable in air for several days. It dissolves in dilute acids, yielding uranous salts. On heating, it is completely converted to the green oxide.

**Uranium Pentoxide,  $\text{U}_2\text{O}_5$ .**—The existence of this oxide is not definitely established. It has been described as the black product obtained when a uranium salt of a volatile acid is strongly ignited in air;<sup>7</sup> when uranyl sulphate,  $(\text{UO}_2)_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , is rapidly heated;<sup>8</sup> when ammonium diuranate,  $(\text{NH}_4)_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ , is heated in a carbon crucible;<sup>9</sup> and when a solution of uranyl nitrate is electrolysed.<sup>10</sup>

<sup>1</sup> Colani, *Compt. rend.*, 1912, 155, 1249.

<sup>2</sup> Raynaud, *loc. cit.*

<sup>3</sup> Smith and Shinn, *Zeitsch. anorg. Chem.*, 1894, 7, 47.

<sup>4</sup> Samsonow, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 96.

<sup>5</sup> Isambert, *Compt. rend.*, 1875, 53, 1087.

<sup>6</sup> Aloy, *Bull. Soc. chim.*, 1899, [3], 21, 613.

<sup>7</sup> Péligot, *Ann. Chim. Phys.*, 1842, [3], 5, 5, 12.

<sup>8</sup> O. de Coninck, *ibid.*, 1903, [7], 28, 5.

<sup>9</sup> Janda, *Oesterr. Z. Berg.-Hüttenw.*, 49, 325, 340; *Jahresber.*, 1901, ii., 266.

<sup>10</sup> O. de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, p. 321.

Many observers regard the substance as a mixture of uranous oxide and urano-uranic oxide,<sup>1</sup> but from a study of the dissociation tension of the latter oxide Schwarz<sup>2</sup> gained evidence of the existence of an intermediate oxide, and by heating the higher oxide in a stream of carbon dioxide in an electric furnace at 1122° C. he obtained a black product of the approximate composition  $U_2O_5$ . The substance is reduced to uranous oxide by strongly heating in hydrogen. It dissolves in acids to form uranous and uranyl salts.

**Urano-uranic Oxide, the Green Oxide of Uranium,  $U_3O_8$  or  $UO_2 \cdot 2UO_3$ ,** occurs in nature in a more or less pure condition as pitchblende (see p. 272). It may be obtained by heating to redness any of the other oxides of uranium;<sup>3</sup> by strongly igniting, at a temperature above 900° C.,<sup>4</sup> ammonium diuranate; or by heating to redness the uranium salt of any volatile acid. The uranyl salts of commerce are invariably impure with alkali, so that it is impossible to obtain the pure oxide from them, unless they are first purified by a series of recrystallisations.<sup>5</sup> To obtain pure urano-uranic oxide, free from alkali, the following method may be used:<sup>6</sup> Sodium uranyl acetate (100 g.) is dissolved in a mixture of water (4 l.) and hydrochloric acid (50 c.c.), and precipitated by adding concentrated ammonia solution (300 c.c.). The precipitate is washed ten times with a 2 per cent. ammonium chloride solution, and then redissolved in hydrochloric acid. The precipitation with ammonia and washing are repeated twice, and the final precipitate, on calcination, yields pure urano-uranic oxide.

Urano-uranic oxide is an amorphous powder, varying in colour, according to its mode of preparation, from green to black, but in all cases it leaves a green streak on unglazed porcelain.<sup>7</sup> The density, according to Karsten, is 7.193; according to Ebelmen,<sup>8</sup> 7.31. The specific heat at ordinary temperatures is 0.07979,<sup>9</sup> but the value falls considerably at lower temperatures, as shown by the following determinations:<sup>10</sup>

Temperature Range, ° C.	Specific Heat.
0 to — 77	0.0616
—77 to —190	0.0428

The oxide is paramagnetic, the susceptibility<sup>11</sup> being  $+0.95 \times 10^{-6}$ , a

<sup>1</sup> See Zimmermann, *Annalen*, 1886, **232**, 273; Colani, *Ann. Chim. Phys.*, 1907, [8], **12**, 59.

<sup>2</sup> Schwarz, *Helv. Chim. Acta*, 1920, **3**, 330.

<sup>3</sup> McCoy and Ashman, *Amer. J. Sci.*, 1908, [4], **26**, 521; Jolibois and Bossuet, *Compt. rend.*, 1922, **174**, 386.

<sup>4</sup> Colani, *Ann. Chim. Phys.*, 1907, [8], **12**, 59.

<sup>5</sup> McCoy and Ashman, *loc. cit.*; Giolitti and Tavanti, *Gazzetta*, 1908, **38**, ii., 239.

<sup>6</sup> Giolitti and Tavanti, *loc. cit.*

<sup>7</sup> Remelé, *Pogg. Annalen*, 1865, **124**, 126; *Zeitsch. anal. Chem.*, 1865, **4**, 379; von der Pfordten, *Annalen*, 1883, **222**, 142; Zimmermann, *ibid.*, 1886, **232**, 273.

<sup>8</sup> Ebelmen, *Ann. Chim. Phys.*, 1842, [3], **5**, 189; *Annalen*, 1842, **43**, 286.

<sup>9</sup> Donath, *Ber.*, 1879, **12**, 742.

<sup>10</sup> Russell, *Physikal. Zeitsch.*, 1912, **13**, 59.

<sup>11</sup> Wedekind and Horst, *Ber.*, 1915, **48**, 105; Honda, see Wedekind, *Magnetochemie*, by Bornträger, p. 76, Berlin, 1911.

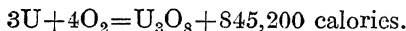
value very near to that for the metal itself. The single electrode potential of the oxide, measured by pasting it in a finely powdered condition with gelatin on a platinum electrode and immersing it in a solution of uranyl nitrate containing 14.3 grams per litre, is :<sup>1</sup>

$$\text{U}_3\text{O}_8/\text{UO}_2(\text{NO}_3)_2 = 0.776 \text{ volt.}$$

This value is identical with that obtained for uranous oxide.

Urano-uranic oxide is insoluble in water and in dilute acids; in concentrated mineral acids it dissolves slowly, forming a mixture of uranous and uranyl salts. It is very stable at high temperatures, and for this reason uranium is usually converted into this oxide for gravimetric estimation. It may be heated in a vacuum for three hours at 1000° C. without any appreciable loss of oxygen, and in order to obtain the dioxide from it by simple dissociation a temperature of 2000° C. is necessary.<sup>2</sup> It is reduced when heated in hydrogen, the sole product being the dioxide (see p. 300). The action commences at about 625° C. and can be completed at 650° C. It also yields the dioxide when heated with sulphur. It is reduced to the metal by heating with carbon in the electric furnace; also by heating with magnesium<sup>3</sup> (see p. 278). When heated in a stream of carbon dioxide at about 1120° C. it yields the pentoxide.<sup>4</sup>

The heat of formation of the oxide has been determined by Mixer<sup>5</sup> as follows :



The chemical behaviour of urano-uranic oxide indicates the presence of tetra- and hexa-valent uranium and supports the view that it is an association of uranous and uranic oxides, thus:  $\text{UO}_2 \cdot 2\text{UO}_3$ . The properties of the substance do not support the view of Groth that it is uranous uranate,  $\text{U}(\text{UO}_4)_2$ .

The oxide is sometimes used for producing a black glaze on porcelain. In uniform films it may be used as a standard of  $\alpha$ -ray activity.<sup>6</sup>

*Hydrates of Urano-uranic Oxide.*—When an aqueous solution of uranyl oxalate, or an alcoholic solution of uranyl acetate, is exposed to sunlight, a violet precipitate of hydrated urano-uranic oxide is formed.<sup>7</sup> Moreover, any uranyl salt in solution in presence of a readily oxidisable organic substance, such as alcohol, ether, or glucose, when exposed to light, or better to ultra-violet rays, yields a violet precipitate which invariably contains the acid present in the original salt. The acid, however, can be removed by boiling with water, and a green hydrated oxide,  $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ , results<sup>8</sup> (see p. 287). Similar violet compounds are also obtained, without the action of light, whenever uranous and

<sup>1</sup> Pierlé, *J. Physical Chem.*, 1919, 23, 517.

<sup>2</sup> Jolibois and Bossuet, *Compt. rend.*, 1922, 174, 386. The oxygen-dissociation pressures *in vacuo*, at temperatures between 625° C. and 1165° C., have been determined by Colani, see *Ann. Chim. Phys.*, 1907, [8], 12, 59.

<sup>3</sup> Aloy, *Bull. Soc. chim.*, 1901, [2], 25, 344; Rideal, *J. Soc. Chem. Ind.*, 1914, 33, 673.

<sup>4</sup> Schwarz, *Helv. Chim. Acta*, 1920, 3, 330.

<sup>5</sup> Mixer, *Amer. J. Sci.*, 1912, [4], 34, 141.

<sup>6</sup> McCoy and Ashman, *Amer. J. Sci.*, 1908, [4], 26, 521.

<sup>7</sup> Ebelmen, *Annalen*, 1842, 43, 286; *Ann. Chim. Phys.*, 1842, [3], 5, 189; Aloy, *Bull. Soc. chim.*, 1900, [3], 23, 368.

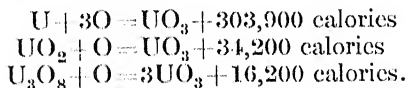
<sup>8</sup> Aloy and Rodier, *Bull. Soc. chim.*, 1920, [4], 27, 101; Aloy and Valdiguié, *Compt. rend.*, 1923, 176, 1229.

uranyl salts are present together in neutral or feebly acid solution at the requisite temperature.

**Uranium Trioxide, Uranic Oxide, Uranic Anhydride, or Uranyl Oxide,  $\text{UO}_3$ ,** is obtained when uranic acid, ammonium diuranate, or ammonium uranyl carbonate is heated to a temperature not exceeding  $300^\circ \text{C}$ .<sup>1</sup> When uranyl nitrate is similarly heated the product always contains basic nitrate,<sup>2</sup> but if this product is heated in a current of oxygen at  $500^\circ \text{C}$ . it yields pure uranium trioxide.<sup>3</sup>

The oxide appears to exist in two modifications, orange-yellow and red, the latter probably being a polymeride of the former.<sup>4</sup> The yellow variety produces the red on prolonged heating. Both forms are amorphous.<sup>5</sup> The oxide is paramagnetic, the susceptibility<sup>6</sup> being  $+1.08 \times 10^{-6}$ . When strongly heated in air or oxygen it yields the green oxide,  $\text{U}_3\text{O}_8$ , and in the latter case traces of ozone are also formed.<sup>7</sup> It is reduced when heated with hydrogen to uranous oxide;<sup>8</sup> with carbon in the electric furnace at  $3000^\circ \text{C}$ . it yields the metal.<sup>9</sup>

The following values for the heat of formation of uranium trioxide have been determined<sup>10</sup> as follows:



Uranium trioxide is slightly basic, but with the exception of uranium hexafluoride, the salts formed by interaction with acids still contain two-thirds of its oxygen in the form of the uranyl radical, compounds of the type  $\text{UO}_2\text{R}'_2$  being produced. On the other hand, however, the oxide acts towards strong bases as an acid anhydride, similar to chromic anhydride, and produces stable uranates. In contact with water it readily forms uranic acid,  $\text{UO}_2(\text{OH})_2$ .<sup>3</sup>

*Hydrates of Uranium Trioxide.*—Two well-defined hydrates are known:<sup>11</sup> (1) the *monohydrate*,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ ; and (2) the *dihydrate*,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ . The former is also known as *uranic acid*,  $\text{H}_2\text{UO}_4$ , or uranyl hydroxide,  $\text{UO}_2(\text{OH})_2$ , and acts both as an acid and a base. It may be obtained in the amorphous condition by heating an alcoholic solution of uranyl nitrate for some time at a temperature just below its boiling-point, and then washing the yellow precipitate produced with boiling water;<sup>12</sup> by exposing a solution of uranium oxalate to light until the

<sup>1</sup> Ebelmen, *loc. cit.*; Liénau, *Beiträge zur Kenntnis der Uranylsalze*, Dissertation, Berlin, 1898; Brunck, *Zeitsch. anorg. Chem.*, 1895, **10**, 222.

<sup>2</sup> Brunck, *loc. cit.*; Lebeau, *Compt. rend.*, 1912, **154**, 1808. Cf. Jacquelin, *Chem. Pharm. Centr.*, 1845, p. 193; de Forcrand, *Compt. rend.*, 1913, **156**, 1954.

<sup>3</sup> Lebeau, *loc. cit.*

<sup>4</sup> O. de Coninck, *Compt. rend.*, 1901, **132**, 204; *Bull. Soc. roy. Belg.*, 1904, pp. 363, 448. See also de Forcrand, *loc. cit.*

<sup>5</sup> See Goldschmidt and Thomassen, *Videnskapsselskapets Skrifter. Mat. Naturv. Klasse*, 1923, p. 5; *Chem. Zentr.*, 1923, **i**, 1149.

<sup>6</sup> Wedekind and Horst, *Ber.*, 1915, **48**, 105.

<sup>7</sup> Brunck, *loc. cit.*

<sup>8</sup> Sabatier and Senderens, *Bull. Soc. chim.*, 1895, [3], **13**, 870; *Compt. rend.*, 1895, **120**, 618.

<sup>9</sup> Moissan, *Compt. rend.*, 1892, **115**, 1031.

<sup>10</sup> Mixer, *Amer. J. Sci.*, 1912, [4], **34**, 141. See also de Forcrand, *loc. cit.*

<sup>11</sup> See Hüttig and von Schroeder, *Zeitsch. anorg. Chem.*, 1922, **121**, 243.

<sup>12</sup> Malaguti, *Ann. Chim. Phys.*, 1843, [3], **9**, 463; see also Berzelius, *Jahresber.*, 1845, **24**, 118.



precipitated violet hydroxide turns yellow,<sup>1</sup> and then washing and drying the product; or by heating the dihydrate,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , in dry air at  $80^\circ \text{C}$ .<sup>2</sup> It is also obtained in the crystalline form by exposing the violet hydrate to air, and then boiling it with water for several hours;<sup>3</sup> by heating a 2 per cent. solution of uranyl acetate in a sealed tube at  $175^\circ \text{C}$ . for 100 hours;<sup>4</sup> by digesting precipitated copper hydrate with a solution of uranyl nitrate;<sup>5</sup> by dissolving the amorphous form in a concentrated solution of uranyl nitrate, evaporating to dryness, and extracting the residue with dry ether; or by the electrolysis of a solution of uranyl nitrate with current intensity less than 1 ampère.<sup>6</sup> It is also formed, mixed with the dihydrate, when a solution of uranyl nitrate is evaporated almost to dryness on a water-bath.<sup>7</sup>

Uranic acid, when amorphous, is a yellow powder, of density 5.92. In the crystalline form it yields, according to its mode of formation, rectangular orthorhombic tables<sup>3</sup> or hexagonal crystals.<sup>4</sup> When heated to  $300^\circ \text{C}$ . it loses water,<sup>1</sup> but it does not appear to be completely dehydrated until it begins to lose oxygen.<sup>8</sup>

The single potential of the acid electrode, determined in the manner described for the green oxide (see p. 304), is as follows: <sup>9</sup>

$$\text{UO}_3 \cdot \text{H}_2\text{O} / \text{UO}_2(\text{NO}_3)_2 = -0.860 \text{ volt.}$$

It dissolves in acids to form yellow solutions which on concentration yield well-crystallised uranyl salts,<sup>10</sup> while with inorganic and organic bases it yields uranates.

The dihydrate,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , appears to be analogous to the corresponding tungsten compound, and behaves as the monohydrate of uranic acid,  $\text{H}_2\text{UO}_4 \cdot \text{H}_2\text{O}$ . It is formed by the slow oxidation in air of the violet hydrate (p. 304);<sup>11</sup> by boiling a solution of ammonium uranyl carbonate, when it falls as a yellow precipitate; by evaporating a solution of uranyl nitrate at ordinary temperature over sulphuric acid, and extracting the residue with ether;<sup>12</sup> or by heating uranous oxide with a solution of hydrogen peroxide.<sup>13</sup> The hydrate is a lemon-yellow powder, lighter in colour than uranic acid. It may be obtained in hexagonal prisms. On heating at  $80^\circ \text{C}$ . in dry air, it yields the monohydrate. It is very soluble in acids, and reacts in the same way as uranic acid.

The *subhydrate*,  $2\text{UO}_3 \cdot \text{H}_2\text{O}$ , or *pyro-uranic acid*,  $\text{H}_2\text{U}_2\text{O}_7$ , corresponding to the stable diuranates, has not as yet been shown to exist.<sup>14</sup>

*Colloidal Uranic Acid*.—By the addition of potash to a solution of

<sup>1</sup> Ebelmen, *Ann. Chim. Phys.*, 1842, [3], 5, 189; *Annalen*, 1842, 43, 286.

<sup>2</sup> de Forcrand, *Compt. rend.*, 1913, 156, 1954; Ebelmen, *loc. cit.*

<sup>3</sup> Aloy, *Bull. Soc. chim.*, 1900, [3], 23, 368.

<sup>4</sup> Riban, *Compt. rend.*, 1881, 93, 1140.

<sup>5</sup> Mailhe, *Thèse*, Toulouse, 1902.

<sup>6</sup> O. de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, p. 321.

<sup>7</sup> O. de Coninck, *Compt. rend.*, 1909, 148, 1462.

<sup>8</sup> Malaguti, *Ann. Chim. Phys.*, 1843, [3], 9, 463.

<sup>9</sup> Pierlé, *J. Physical Chem.*, 1919, 23, 517.

<sup>10</sup> Ley, *Ber.*, 1900, 33, 2659; Bruner, *Zeitsch. Chem. Phys. Math.*, 1900, 32, 133. Compare Kohlschütter, *Annalen*, 1901, 314, 311. The heats of solution of the hydrate in the chief mineral acids have been determined by Aloy, *Compt. rend.*, 1896, 122, 1541; see also de Forcrand, *ibid.*, 1913, 156, 1954.

<sup>11</sup> Ebelmen, *loc. cit.* Compare Aloy's method for the monohydrate, above.

<sup>12</sup> Lebeau, *Compt. rend.*, 1912, 154, 1808.

<sup>13</sup> O. de Coninck, *ibid.*, 1911, 153, 63.

<sup>14</sup> Cf. Hüttig and von Schroeder, *Zeitsch. anorg. Chim.*, 1922, 121, 243.

uranyl nitrate or chloride in the presence of sugar, Graham <sup>1</sup> obtained, in the cold, a deep orange-yellow coloured solution, from which all acid and alkali could be removed by dialysis. The solution contained hydrated uranic oxide, and showed considerable stability. It coagulated, however, on the addition of an electrolyte. Szilárd <sup>2</sup> prepared a similar solution by gradually adding uranic acid to a hot dilute solution of uranyl nitrate until the former is no longer dissolved. The resulting solution contained a little uranyl nitrate, but was very stable. Colloidal uranic acid may also be obtained <sup>3</sup> by precipitating all the chlorine from an aqueous solution of uranyl chloride trihydrate (see p. 297) by means of silver oxide, and dialysing after filtration.

It has been observed <sup>4</sup> that colloidal uranic hydroxide, in very dilute solution, acts as a powerful catalyst in the synthesis of formaldehyde when an aqueous solution of carbon dioxide is exposed to direct sunlight.

### SALTS OF URANIC ACID.

Uranic acid,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ , is a dibasic acid, and yields salts of the type  $\text{R}_2\text{UO}_4$ . As in the case of the corresponding acids of the other elements of the group, in addition to the normal salts, other types, richer in acid content, also exist. For example, salts of the alkali metals of types  $\text{R}_2\text{O} \cdot x\text{UO}_3$ , where  $x$  may be 1, 2, 3, 4, 5, or 6, are known. The acids corresponding to such derivatives have not been isolated. The most important salts are the diuranates, from the hypothetical diuranic or pyro-uranic acid,  $\text{H}_2\text{U}_2\text{O}_7$ , which are usually precipitated when metallic oxides, hydroxides, or carbonates are added to solutions of uranyl salts. The normal uranates are generally obtained by fusion. They are yellow in colour, insoluble in water, but soluble in acids. Salts containing the more electro-positive metals only have been prepared.

**Ammonium Diuranate**,  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ , is obtained as a yellow voluminous precipitate when solutions of uranyl salts are treated with ammonia. It is prepared commercially (see p. 277) by boiling a solution of sodium uranyl carbonate with ammonium sulphate,<sup>5</sup> or by boiling a solution of sodium diuranate with concentrated ammonium chloride solution. It is a deep yellow powder, which may be dried at  $100^\circ \text{C}.$ ; at higher temperatures it yields urano-uranic oxide. When fused with ammonium chloride, uranous oxide is formed. It is known commercially as "uranium yellow" (see also sodium diuranate) and is used in making fluorescent "uranium glass." It is insoluble in ammonium hydroxide solution, and this fact is sometimes made use of (see p. 338) in the analytical separation of uranium.

**Ammonium Hexa-uranate**,  $(\text{NH}_4)_2\text{U}_6\text{O}_{19} \cdot 10\text{H}_2\text{O}$ , separates as a yellow microcrystalline powder when an aqueous solution of ammonium uranyl acetate is boiled for a considerable time.<sup>6</sup> The compound decomposes on heating, yielding ammonia and the green oxide.

**Hydroxylamine Uranate.**—When an aqueous solution of uranyl

<sup>1</sup> Graham, *Phil. Trans.*, 1861, 151, i., 183; *Jahresber.*, 1861, p. 63.

<sup>2</sup> Szilárd, *J. Chim. phys.*, 1907, 5, 488, 636.

<sup>3</sup> Mylius and Dietz, *Ber.*, 1901, 34, 2774.

<sup>4</sup> Moore and Webster, *Proc. Roy. Soc.*, 1913, B, 87, 163.

<sup>5</sup> See also Stolba, *Zeitsch. anal. Chem.*, 1864, 3, 74.

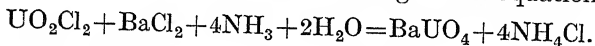
<sup>6</sup> Zehenter, *Monatsh.*, 1900, 21, 235.

nitrate (20 grams) and hydroxylamine hydrochloride (10 grams) is treated with 100 c.c. of 7 per cent. ammonia solution, the ammonium diuranate first formed redissolves, and a canary-yellow crystalline powder of composition  $(\text{NH}_3\text{OH})_2\text{UO}_4 \cdot 2\text{NH}_3$  is obtained on allowing to crystallise.<sup>1</sup> This compound is stable at ordinary temperatures, begins to lose ammonia when heated above  $70^\circ \text{C}.$ , and if heated cautiously to  $120^\circ \text{C}.$  yields uranic acid,  $\text{H}_2\text{UO}_4$ . If allowed to remain in contact with cold water for some hours, or if treated with hot water, it yields hydroxylamine uranate,  $(\text{NH}_3\text{OH})_2\text{UO}_4 \cdot \text{H}_2\text{O}$ . The latter is also formed when the ammonio compound is heated at  $100^\circ \text{C}.$  with glycerol, or treated with acetic acid (2 molecules), excess being avoided; or when freshly precipitated alkali diuranates are acted upon by hydroxylamine hydrochloride.<sup>2</sup>

Hydroxylamine uranate forms well-defined yellowish-green crystals, which, when slowly heated at  $125^\circ \text{C}.$ , lose water and ammonia and leave a residue of uranic acid containing, according to Kohlschütter and Vogdt, nitrogen and nitrous oxide in solution, these gases escaping when the residue is dissolved in dilute acids. Friedheim, however, suggests that the residue consists of uranic acid and what may be considered as an anhydride of the uranate,  $\text{UO}_2(\text{NH}_3\text{O})_2$ , which on treating with acid yields ammonia, nitrogen, and nitrous oxide.<sup>3</sup> The uranate readily reduces Fehling's solution.

**Hydroxylamine Potassio-uranate**,  $(\text{NH}_3\text{OH})(\text{NH}_3\text{OK})\text{UO}_4 \cdot \text{H}_2\text{O}$ , is formed<sup>4</sup> when a 10 per cent. caustic potash solution is added to a solution containing uranyl nitrate and hydroxylamine hydrochloride until the precipitate first formed is redissolved. Reddish-yellow cubic crystals separate slowly from the liquid. The corresponding sodium compound,  $(\text{NH}_3\text{OH})(\text{NH}_3\text{ONa})\text{UO}_4 \cdot \text{H}_2\text{O}$ , yields minute prismatic crystals, while the mother-liquor, on further concentration, deposits orange-red prisms of the salt,  $(\text{NH}_3\text{ONa})_2\text{UO}_4 \cdot 6\text{H}_2\text{O}$ .

**Barium Uranate**,  $\text{BaUO}_4$ , is formed by fusing together barium chloride and urano-uranic oxide,<sup>5</sup> or by mixing solutions of barium chloride and uranyl chloride and passing in excess of ammonia.<sup>6</sup> The reaction in the latter case proceeds according to the equation:



It yields yellow glistening crystals, insoluble in water, but readily soluble in dilute hydrochloric acid.

**Barium Diuranate**,  $\text{BaU}_2\text{O}_7$ , is obtained by heating barium uranyl acetate,<sup>7</sup> or by heating together the green oxide and barium chlorate. It is obtained in a hydrated condition when ammonia is added to mixed solutions of barium chloride and uranyl nitrate, or when excess of baryta water is added to uranyl nitrate solution. It is a deep yellow crystalline powder.

**Bismuth Uranate**,  $\text{Bi}(\text{OH})\text{UO}_4 \cdot \text{H}_2\text{O}$  or  $\text{Bi}_2\text{O}_3 \cdot 2\text{UO}_3 \cdot 3\text{H}_2\text{O}$ , occurs naturally as *uranosphærite* (see p. 273).

<sup>1</sup> Hofmann, *Zeitsch. anorg. Chem.*, 1897, 15, 75.

<sup>2</sup> Kohlschütter and Vogdt, *Ber.*, 1905, 38, 1419.

<sup>3</sup> Friedheim, *ibid.*, 1905, 38, 2352. Compare Kohlschütter and Vogdt, *ibid.*, [1905, 38, 2992.

<sup>4</sup> Kohlschütter and Hofmann, *Annalen*, 1899, 307, 314.

<sup>5</sup> Ditte, *Compt. rend.*, 1882, 95, 988.

<sup>6</sup> O. de Coninck, *Bull. Acad. roy. Belg.*, 1909, p. 835.

<sup>7</sup> Wertheim, *Ann. Chim. Phys.*, 1844, [3], 11, 49.

**Calcium Uranate**,  $\text{CaUO}_4$ , and calcium diuranate,  $\text{CaU}_2\text{O}_7$ , are similar to the corresponding barium salts and may be prepared by similar methods. The diuranate is highly refractory and does not fuse at red heat.

**Iron Uranate**.—Arfvedson<sup>1</sup> heated in hydrogen the precipitate obtained by passing ammonia into a solution containing ferric and uranyl salts, and obtained a product which he called iron uranate. It appears, however, to be a mixture of the oxides of iron and uranium.

**Lithium Uranate**,  $\text{Li}_2\text{UO}_4$ , is obtained by fusing together lithium chloride and urano-uranic oxide.<sup>2</sup> It is less stable towards water than the other alkali uranates.

**Magnesium Uranate**,  $\text{MgUO}_4$ , and magnesium diuranate,  $\text{MgU}_2\text{O}_7$ , may be obtained by the methods described for the barium salts. The diuranate yields yellowish-green needle-shaped crystals.

The **neodymium salt**,  $\text{Nd}_2(\text{U}_3\text{O}_{10})_3 \cdot 18\text{H}_2\text{O}$ , is formed as a yellow crystalline powder when neodymium hydroxide is heated with a solution of uranyl acetate on a water-bath. Praseodymium hydroxide behaves in the same way.<sup>3</sup>

**Potassium Uranate**,  $\text{K}_2\text{UO}_4$ , is formed by fusing together potassium chloride and urano-uranic oxide.<sup>2</sup> If the operation is performed in a platinum crucible, the heat being applied from below, the uranate separates as a crystalline crust at the surface, and can be removed and washed free from potassium chloride by means of water. It may also be obtained by fusing a mixture of uranyl phosphate and potassium sulphate,<sup>4</sup> or a mixture containing uranyl chloride (6 parts), ammonium chloride (16 parts), and potassium chloride (4 parts);<sup>5</sup> or by heating together uranium trioxide and potassium chlorate.<sup>6</sup> After washing with water, orange-yellow pseudo-hexagonal leaflets remain. The uranate dissolves readily in acids. It may be heated to redness without fusion.

**Potassium Diuranate**,  $\text{K}_2\text{U}_2\text{O}_7$ , is obtained in the anhydrous condition by heating potassium uranyl acetate or carbonate;<sup>7</sup> or by fusing together uranium trioxide and potassium carbonate. It yields glistening crystals, which vary in colour from yellow to orange-red according to the mode of preparation. The *trihydrate*,  $\text{K}_2\text{U}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , is obtained by drying at 100° C. the yellow precipitate formed when excess of potassium hydroxide is added to a solution of a uranyl salt.<sup>8</sup> According to Stolba,<sup>9</sup> if the precipitate is allowed to dry in air at ordinary temperature, the *hexahydrate*,  $\text{K}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ , is formed.

**Potassium Tetra-uranate**,  $\text{K}_2\text{U}_4\text{O}_{13} \cdot 5\text{H}_2\text{O}$ , separates as a yellow powder on evaporating a solution of potassium uranyl acetate.<sup>10</sup>

**Potassium Hexa-uranate**,  $\text{K}_2\text{U}_6\text{O}_{19} \cdot 6\text{H}_2\text{O}$ , results on strongly heating a mixture of uranyl sulphate and potassium chloride;<sup>11</sup> by

<sup>1</sup> Arfvedson, *Pogg. Annalen*, 1824, **1**, 245.

<sup>2</sup> Ditte, *loc. cit.*

<sup>3</sup> Orloff, *Chem. Zeit.*, 1907, **31**, 1119.

<sup>4</sup> Grandeau, *Ann. Chim. Phys.*, 1886, [6], **8**, 233.

<sup>5</sup> Zimmermann, *Annalen*, 1882, **213**, 290.

<sup>6</sup> Brunck, *Zeitsch. anorg. Chem.*, 1895, **10**, 246.

<sup>7</sup> Wertheim, *J. prakt. Chem.*, 1842, **29**, 207.

<sup>8</sup> Patera, *ibid.*, 1850, **51**, 125.

<sup>9</sup> Stolba, *Zeitsch. anal. Chem.*, 1864, **3**, 72.

<sup>10</sup> Zehenter, *Monatsh.*, 1900, **21**, 235.

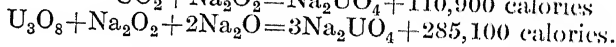
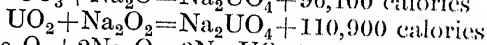
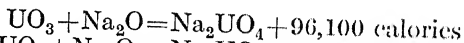
<sup>11</sup> Drenckmann, *Zeitsch. ges. Naturw.*, 1861, **17**, 134.

washing out the melt with boiling water, and drying the residue *in vacuo*, a yellow crystalline powder is obtained. It loses all its water when heated to 300° C. The *decahydrate*,  $K_2U_6O_{19} \cdot 10H_2O$ , may be obtained by boiling a solution of potassium uranyl acetate.<sup>1</sup>

**Rubidium Uranate**,  $Rb_2UO_4$ , is obtained by fusion of rubidium chloride with the green oxide of uranium.<sup>2</sup>

**Silver Diuranate**,  $Ag_2U_2O_7$ , separates as an orange-red precipitate when freshly precipitated silver oxide is added to a solution of uranyl nitrate.<sup>3</sup> It is also formed by the action of potassium uranate on fused silver nitrate.

**Sodium Uranate**,  $Na_2UO_4$ , may be obtained in the amorphous form by heating together urano-uranic oxide and sodium chlorate; or by heating sodium uranyl acetate or carbonate.<sup>4</sup> The crystalline form is produced by adding the green oxide in small quantities to fused sodium chloride,<sup>2</sup> or by dissolving the amorphous form in fused sodium chloride, and allowing crystallisation to take place.<sup>5</sup> It yields reddish-yellow to greenish-yellow prisms or leaflets. The following values for the heat of formation of sodium uranate have been obtained by Mixter: <sup>6</sup>



**Sodium Diuranate**,  $Na_2U_2O_7 \cdot 6H_2O$ , is prepared commercially as already described (see p. 277),<sup>7</sup> and is generally known as "uranium yellow." It may be formed by adding excess of sodium hydroxide to a solution of a uranyl salt, and drying the resulting yellow precipitate in air.<sup>8</sup> When dried over sulphuric acid it loses nearly all its water. It is obtained in the anhydrous condition by heating together uranyl chloride, sodium chloride, and ammonium chloride, or by strongly heating the hexahydrate.

The *uranium yellow* of commerce, which is used in staining and painting glass and porcelain and for making uranium glass (*cf.* ammonium diuranate), is obtained in two colours: light yellow, by decomposing the solution of sodium uranyl carbonate with sulphuric acid, and orange yellow, by decomposing with excess of sodium hydroxide.

**Sodium Triuranate**,  $Na_2U_3O_{10}$ , is formed by heating together uranyl sulphate and sodium chloride, and washing the residue with water<sup>9</sup> (see potassium hexa-uranate). It yields lustrous, golden-yellow, rhombic crystals, of density 6.9, insoluble in water, but soluble in dilute acids.

**Sodium Penta-uranate**,  $Na_2U_5O_{16} \cdot 5H_2O$ , is obtained as an

<sup>1</sup> Zehenter, *Monatsh.*, 1900, 21, 235.

<sup>2</sup> Ditte, *Compt. rend.*, 1882, 95, 988.

<sup>3</sup> Guyard, *Bull. Soc. chim.*, 1864, [2], 1, 69; see also Alibegoff, *Annalen*, 1882, 233, 104, 131, 135.

<sup>4</sup> Wertheim, *J. prakt. Chem.*, 1842, 29, 207.

<sup>5</sup> Zimmermann, *Annalen*, 1882, 213, 290.

<sup>6</sup> Mixter, *Amer. J. Sci.*, 1912, [4], 34, 141.

<sup>7</sup> See also Anthon, *Jahresber.*, 1860, p. 698; Kessler, *ibid.*, 1857, p. 199; Hofmann and Strauss, *Ber.*, 1900, 33, 3126; Metzger and Heidelberger, *J. Amer. Chem. Soc.*, 1909, 31, 1040.

<sup>8</sup> Patera, *Sitzungsber. K. Akad. Wiss. Wien*, 1853, 11, 848; *Jahresber.*, 1853, p. 740.

<sup>9</sup> Drenckmann, *Zeitsch. ges. Naturw.*, 1861, 17, 134.

orange-yellow powder on boiling a solution of sodium uranyl acetate.<sup>1</sup>

**Strontium Uranate**,  $\text{SrUO}_4$ , and strontium diuranate,  $\text{SrU}_2\text{O}_7$ , are similar in properties and are prepared by similar methods to the corresponding barium and calcium salts.

**Zinc Uranate**,  $\text{ZnUO}_4$ , is deposited, according to Wertheim,<sup>2</sup> on a sheet of zinc placed in a solution of uranyl nitrate; or it may be precipitated from a solution of zinc uranyl acetate by the addition of baryta water. It is an amorphous yellow powder, insoluble in water.

#### PERURANIC ACID AND PERURANATES.

The existence of uranium tetroxide, or uranium peroxide,  $\text{UO}_4$ , in the anhydrous condition, has not been established,<sup>3</sup> although Fairley<sup>4</sup> claimed to have obtained it as a heavy crystalline precipitate by adding hydrogen peroxide to a solution of uranyl nitrate in presence of a large excess of sulphuric acid, and allowing the mixture to stand for a few days. The product, when carefully dried, did not lose moisture on heating. It decolorised potassium permanganate solution on warming, and when heated with hydrochloric acid, liberated chlorine.

The hydrate, **peruranic acid**,  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ , is obtained<sup>4</sup> as a yellowish-white precipitate by the addition of dilute hydrogen peroxide to a solution of uranyl nitrate or acetate, excess of the uranyl salt being allowed to remain unacted upon. The precipitate may be dried at  $100^\circ \text{C}$ . without loss of oxygen.<sup>5</sup> The precipitation has been investigated by Mazzucchelli.<sup>6</sup> It is hindered by the presence of chlorides, sulphates, acetates, oxalates, or tartrates, owing to the tendency to form soluble complexes. In presence of alkali or alkaline earth metals no precipitation occurs owing to the formation of soluble peruranates. The precipitate is very slightly soluble in water and in a solution of ammonium chloride. In the former the solubility, expressed in grams of  $\text{UO}_3$  per litre of solution, is 0.0061 at  $20^\circ \text{C}$ . and 0.0084 at  $90^\circ \text{C}$ . When strongly ignited, the hydrate loses water<sup>7</sup> and oxygen, leaving a residue of urano-uranic oxide. It decolorises permanganate in dilute sulphuric acid solution, the ratio of active oxygen to uranium being 1:1.<sup>8</sup>

Peruranates of the alkali metals are obtained by acting on alkaline solutions of uranyl nitrate with hydrogen peroxide. They are soluble in water, but may be precipitated by the addition of alcohol. Corresponding peruranates of the heavier metals may be obtained by double decomposition with solutions of the sodium salt.

The constitution of peruranic acid and of the peruranates is not yet completely understood. Fairley,<sup>4</sup> from a study of the decomposition of the acid by means of alkalis, suggested the formula  $(\text{UO}_3)_2\text{UO}_6$ . It was shown, however, by Melikoff and Pissarjewsky<sup>9</sup> that, by means

<sup>1</sup> Zehenter, *loc. cit.*

<sup>2</sup> Wertheim, *loc. cit.*

<sup>3</sup> See Alibegoff, *Annalen*, 1886, **233**, 117; Hüttig and von Schroeder, *Zeitsch. anorg. Chem.*, 1922, **121**, 243.

<sup>4</sup> Fairley, *Trans. Chem. Soc.*, 1877, **31**, 127.

<sup>5</sup> See also Alibegoff, *loc. cit.*; Pissarjewsky, *Zeitsch. anorg. Chem.*, 1900, **24**, 108. Cf. O. de Coninck, *Bull. Acad. roy. Belg.*, 1909, p. 692.

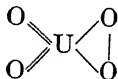
<sup>6</sup> Mazzucchelli, *Atti R. Accad. Lincei*, 1906, [5], **15**, ii., 429, 494.

<sup>7</sup> See Brunck, *Zeitsch. anorg. Chem.*, 1895, **10**, 246.

<sup>8</sup> Pissarjewski, *loc. cit.*

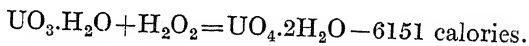
<sup>9</sup> Melikoff and Pissarjewsky, *Ber.*, 1897, **30**, 2902.

of aluminium hydroxide, the alkali peruranates could be quantitatively resolved into the alkali peroxides and uranium tetroxide. This reaction is more in accordance with the constitution, for example, for the sodium salt,  $(\text{Na}_2\text{O}_2)_2\text{UO}_4$ . Moreover, carbon dioxide, which has no action on uranic acid, converts insoluble peruranates into metallic hydrogen carbonates, hydrogen peroxide, and free peruranic acid, again supporting the formula  $(\text{R}\cdot\text{O}_2)_2\text{UO}_4$ . The action of alkali on the peracid, the latter being partially reduced to uranium trioxide, whilst the alkali peroxide is formed, is also in agreement with such formulation. These considerations lead to the suggestion that the tetroxide is a peroxide of the hydrogen peroxide type, probably



and that the peruranates, instead of being salts of a peruranic acid, are probably additive compounds of the tetroxide with metallic peroxides.<sup>1</sup>

The following value for the heat of formation of peruranic acid has been obtained :<sup>2</sup>



By drying the precipitate of the dihydrate at ordinary temperatures Fairley<sup>3</sup> obtained a product which he considered to be a *tetrahydrate*,  $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ , but it has not been established that this is a definite chemical compound. Hüttig and von Schroeder<sup>4</sup> also describe a bright yellow hygroscopic trihydrate,  $\text{UO}_4 \cdot 3\text{H}_2\text{O}$ , which, when heated, loses oxygen before all the water is expelled. If heated in a vacuum, it yields the trioxide, not the tetroxide. By means of the Hüttig tensi-eudiometer these investigators also obtained indications of the following hydrates :  $\text{UO}_3 \cdot \text{H}_2\text{O}_2 \cdot 3 \cdot 5\text{H}_2\text{O}$  ;  $2\text{UO}_3 \cdot \text{H}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$  ;  $2\text{UO}_3 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ .

**Ammonium Peruranate**,  $(\text{NH}_4)_2\text{O}_2 \cdot (\text{UO}_4)_2 \cdot 8\text{H}_2\text{O}$ , is obtained by the action of hydrogen peroxide and excess of ammonia on a solution of uranyl nitrate ; on the addition of alcohol it separates as an orange-yellow crystalline precipitate.

**Barium Peruranates** : (i)  $(\text{BaO}_2)_2 \cdot \text{UO}_4 \cdot 8\text{H}_2\text{O}$  is obtained by double decomposition of the sodium salt with barium chloride. It is an orange-coloured crystalline powder. (ii)  $\text{BaO}_2 \cdot (\text{UO}_4)_2 \cdot 9\text{H}_2\text{O}$  is obtained in the same way from ammonium peruranate solutions as a yellow flocculent precipitate.

**Calcium Peruranate**,  $(\text{CaO}_2)_2 \cdot \text{UO}_4 \cdot 10\text{H}_2\text{O}$ , is obtained in a similar way to the corresponding barium compound, as also is

**Copper Peruranate**,  $(\text{CuO}_2)_2 \cdot \text{UO}_4$  (?).

**Lead Peruranate**,  $(\text{PbO}_2)_2 \cdot \text{UO}_4 + \text{PbO} \cdot \text{UO}_3$ , separates as a deep orange-coloured crystalline precipitate when lead acetate is added to a solution of the sodium salt. This compound is not of the usual type, since there is no peroxide oxygen attached to the lead.

<sup>1</sup> The investigations by Melikoff and Pissarjewsky also concern permolybdates (see p. 156), pertungstates (see p. 242), and pertitanates (see Vol. V.). See also Price, *Peracids and their Salts*, Longmans, 1912.

<sup>2</sup> Pissarjewsky, *Zeitsch. anorg. Chem.*, 1900, 24, 101.

<sup>3</sup> Fairley, *Trans. Chem. Soc.*, 1877, 31, 127.

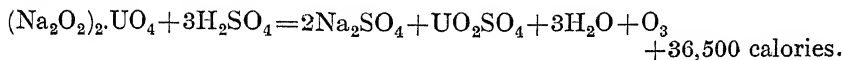
<sup>4</sup> Hüttig and von Schroeder, *Zeitsch. anorg. Chem.*, 1922, 121, 243.

**Lithium Peruranate**,  $\text{Li}_2\text{O}_2 \cdot (\text{UO}_4)_2 \cdot 8\text{H}_2\text{O}$ , is obtained by treating a solution of uranyl nitrate with lithium hydroxide and hydrogen peroxide, and then precipitating with alcohol. It yields minute, pale yellow crystals. An unstable compound,  $(\text{Li}_2\text{O}_2)_2\text{UO}_4$ , has also been obtained.

**Nickel Peruranate**,  $(\text{NiO})_2 \cdot \text{UO}_4$ , resembles the lead compound, and is precipitated when nickel sulphate is added to a solution of the sodium salt.

**Potassium Peruranate**,  $(\text{K}_2\text{O}_2)_2 \cdot \text{UO}_4$ , is obtained by adding hydrogen peroxide to a solution of uranic acid or peruranic acid in aqueous caustic potash, and precipitating by means of alcohol. The salt is less stable than the corresponding sodium compound.<sup>1</sup> Red peruranates of composition  $\text{K}_2\text{UO}_5$  and  $\text{K}_2\text{UO}_5 \cdot 3\text{H}_2\text{O}$  have been described.<sup>2</sup>

**Sodium Peruranates.**—The compound  $(\text{Na}_2\text{O}_2)_2 \cdot \text{UO}_4 \cdot 8\text{H}_2\text{O}$  is prepared in the same way as the potassium salt. It gradually separates from the concentrated solution without the addition of alcohol, and forms yellow needle-shaped crystals. If only a small quantity of the alkali is present, the addition of alcohol first precipitates a deep red oil which gradually becomes crystalline and has the composition  $\text{Na}_2\text{O}_2 \cdot (\text{UO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The solution of sodium peruranate gradually undergoes decomposition, hydrogen peroxide being liberated.<sup>3</sup> Like most peruranates, it yields ozonised oxygen when treated with concentrated sulphuric acid. The following thermal value for the reaction has been given :<sup>4</sup>



A salt of composition,  $\text{Na}_2\text{UO}_5 \cdot 5\text{H}_2\text{O}$ , has been prepared.<sup>5</sup>

*Complex derivatives* of uranium tetroxide with salts of both inorganic and organic acids have been described.<sup>6</sup> When a solution containing equivalent quantities of sodium pyrophosphate and sodium uranyl pyrophosphate is treated with hydrogen peroxide the compound  $\text{Na}_4\text{P}_2\text{O}_7 \cdot (\text{UO}_4)_2 \cdot 18\text{H}_2\text{O}$  is obtained ; similarly a solution of ammonium uranyl carbonate yields the compound  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{UO}_4 \cdot 2\text{H}_2\text{O}$ .

A *peroxyfluoride*,  $3(\text{UO}_4 \cdot \text{KF}) \cdot \text{UO}_3\text{F}_2 \cdot \text{KF} \cdot 4\text{H}_2\text{O}$ , has also been obtained (see p. 293).

## URANIUM AND SULPHUR.

Three well-defined sulphides of uranium are known :

**Uranium Monosulphide**,  $\text{US}$ , is a black amorphous powder obtained by heating the sesquisulphide in hydrogen.<sup>7</sup>

**Uranium Sesquisulphide**,  $\text{U}_2\text{S}_3$ , is obtained in greyish-black needle-shaped crystals when uranium tribromide is heated in hydrogen

<sup>1</sup> Cf. Abegg-Auerbach, *Handbuch der anorganischen Chemie*, Leipzig, 1921, IV., 1, ii., 964.

<sup>2</sup> O. de Coninck, *Compt. rend.*, 1909, 148, 1769 ; Aloy, *Bull. Soc. chim.*, 1902, [3], 27, 734 ; 1903, [3], 29, 292.

<sup>3</sup> Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 472.

<sup>4</sup> Pissarjewsky, *Zeitsch. anorg. Chem.*, 1900, 24, 101.

<sup>5</sup> Aloy, *loc. cit.*

<sup>6</sup> Mazzucchelli and Bimbi, *Atti R. Accad. Lincei*, 1907, [5], 16, ii., 576.

<sup>7</sup> Alibegoff, *Annalen*, 1886, 233, 131, 135.



sulphide until evolution of hydrogen bromide ceases.<sup>1</sup> It is readily oxidised in air, but is resistant to dilute acids. Concentrated nitric acid reacts violently, causing deflagration.

**Uranium Disulphide, Uranous Sulphide,  $US_2$ ,** is formed when metallic uranium is heated in sulphur vapour at  $500^\circ C.$ ; at higher temperatures the uranium burns, yielding the same product. It is also produced when uranous chloride is heated to redness in a current of hydrogen sulphide;<sup>2</sup> or better, by heating the less volatile double chloride,  $Na_2UCl_6$ , in carefully dried hydrogen sulphide,<sup>3</sup> or hydrogen laden with sulphur vapour, the disulphide being separated from sodium chloride by rapidly washing the product in cold boiled water; or the sodium uranium chloride may be fused with certain sulphides, preferably stannous sulphide, but those of sodium, aluminium, magnesium, or antimony may be used, in a slow stream of dry hydrogen. If moisture is not rigorously excluded in these operations some uranyl sulphide is formed.

Uranium disulphide obtained from uranous chloride is a greyish-black amorphous powder. As prepared by Colani from the double chloride, it yields black to iron-grey lustrous crystals belonging to the tetragonal system,  $a:c=1:0.6152$ . It may be heated to  $1000^\circ C.$  without decomposition or fusion. It oxidises in air to uranyl sulphide, and deflagrates at higher temperatures. It is decomposed by steam at red heat. It is fairly stable towards cold water, but is rapidly decomposed by dilute acids, nitric acid reacting very violently with formation of uranyl sulphate.

A hydrated uranium disulphide is obtained as a black precipitate when a solution of a uranous salt is treated with an alkali sulphide. It is unstable and oxidises on exposure to air.

**Uranium Oxysulphide,  $U_3O_2S_4$  or  $UO_2 \cdot 2US_2$ ,** is formed<sup>4</sup> when uranous oxide, urano-uranic oxide, or ammonium uranate is heated in a stream of hydrogen sulphide or carbon disulphide vapour; when one of the oxides is heated with a mixture of ammonium chloride and sulphur; or when uranyl sulphate is heated in hydrogen or with potassium pentasulphide. It is a greyish-black powder, which is decomposed by nitric acid with deposition of sulphur.

**Uranyl Sulphide,  $UO_2S$ ,** is obtained by adding ammonium sulphide to an alcoholic solution of a uranyl salt, washing the precipitate with alcohol and drying in a vacuum. Precipitation from aqueous solutions yields a brown amorphous hydrated form, which is soluble in dilute acids, including acetic acid, and also in ammonium carbonate.<sup>5</sup> Complete precipitation is obtained only after prolonged warming of the mixture containing a slight excess of ammonium sulphide; the precipitate then becomes olive green, crystalline, and can be easily filtered, but it consists largely of hydrated uranous oxide and sulphur, due to hydrolytic decomposition by the warm water. Uranyl sulphide is obtained as black, tetragonal, needle-shaped crystals by fusing together pure dry potassium thiocyanate (12 parts), urano-uranic oxide (8

<sup>1</sup> Alibegoff, *Annalen*, 1886, 233, 131, 135.

<sup>2</sup> Hermann, *Uranverbindungen*, Göttingen, 1861, p. 18; *Jahresber.*, 1861, p. 258.

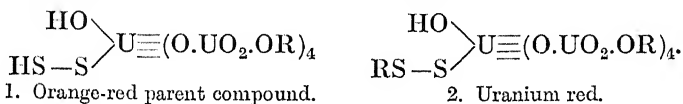
<sup>3</sup> Colani, *Compt. rend.*, 1903, 137, 382; *Ann. Chim. Phys.*, 1907, [8], 12, 59.

<sup>4</sup> Rose, *Gilbert's Annalen*, 1823, 73, 139; Hermann, *Jahresber.*, 1861, p. 260.

<sup>5</sup> Remelé, *Compt. rend.*, 1864, 58, 716; *Pogg. Annalen*, 1865, 124, 126; *Zeitsch. anal. Chem.*, 1865, 4, 379; Zimmermann, *Annalen*, 1880, 204, 204.

parts), and flowers of sulphur (5 parts).<sup>1</sup> It rapidly decomposes on heating, leaving a residue of the green oxide.

If uranyl sulphide, freshly precipitated from aqueous solution, is digested for two days with excess of ammonium sulphide, the mixture being in contact with air, a deep red solid of complex composition, and known as *uranium red* is produced.<sup>2</sup> It has been shown by Kohlschütter<sup>3</sup> that a series of similar red compounds may be obtained by reducing solutions of alkali uranates, containing excess of uranyl sulphate or nitrate and a little free alkali, by means of hydrogen sulphide; in each case an orange-yellow compound is first produced, which on treatment with alkali yields a blood-red *uranium red*. This is decomposed by acids, with liberation of hydrogen sulphide and sulphur. The composition of the orange-yellow substance appears to be  $5\text{UO}_3 \cdot 2\text{K}_2\text{O} \cdot \text{H}_2\text{S}_2$ , while that of the potassium uranium-red corresponds to  $5\text{UO}_3 \cdot 2\text{K}_2\text{O} \cdot \text{HKS}_2$ . Thus all the uranium is in the hexavalent condition, and from a study of the two compounds on decomposition, Kohlschütter suggests the following constitutional formulæ:



**Uranium Sulphite.**—The existence of normal uranous sulphite has not been established. The addition of a saturated solution of an alkali sulphite to uranous chloride solution precipitates a greyish-green basic sulphite of composition  $\text{UO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ .<sup>4</sup> When solutions of uranyl salts are treated with sodium bisulphite, a reddish-brown precipitate is produced which dissolves in excess of the reagent; by boiling such solutions the above basic sulphite is again precipitated.<sup>5</sup> It is insoluble in water, but dissolves in a solution of sulphurous acid.

**Uranyl Sulphite.**—The addition of ammonium sulphite to a solution of uranyl nitrate yields a yellow flocculent precipitate to which Muspratt<sup>6</sup> gave the formula  $\text{UO}_2\text{SO}_3 \cdot 3\text{H}_2\text{O}$ . It contains, however, some ammonium uranate.<sup>7</sup> A crystalline hydrate,  $\text{UO}_2\text{SO}_3 \cdot 4\text{H}_2\text{O}$ , is obtained by evaporating a solution of uranic acid in aqueous sulphurous acid, or by passing sulphur dioxide into an aqueous solution of uranyl nitrate or acetate.<sup>8</sup> It separates in pale green needles, which are insoluble in water but dissolve in aqueous or alcoholic sulphurous acid. When heated to  $105^\circ \text{C}$ . it loses seven-eighths of its water. This fact led Kohlschütter<sup>3</sup> to suggest that it was a complex uranyl compound of composition  $\text{O}(\text{UO}_2 \cdot \text{SO}_3\text{H})_2 \cdot 7\text{H}_2\text{O}$ , but this view is not borne out by conductivity measurements.<sup>9</sup>

<sup>1</sup> Milbauer, *Zeitsch. anorg. Chem.*, 1904, 42, 448.

<sup>2</sup> Patera, *J. prakt. Chem.*, 1850, [1], 51, 122; Remelé, *Ann. Phys. Chem.*, 1864, [2], 124, 114; 1865, 125, 209; *Pogg. Annalen*, 1865, 124, 158; Hermann, *Jahresber.*, 1861, p. 14; Zimmermann, *loc. cit.*

<sup>3</sup> Kohlschütter, *Annalen*, 1901, 314, 311. For similar compounds with hydrazine, see Salvadori, *Atti R. Accad. Lincei*, 1912, [5], 21, ii, 455.

<sup>4</sup> Röhrig, *J. prakt. Chem.*, 1888, 37, 239; Rammelsberg, *Pogg. Annalen*, 1842, 55, 318; 56, 125; 1843, 59, 1; *Ber.*, 1872, 5, 1003.

<sup>5</sup> Brunck, *Annalen*, 1904, 336, 281.

<sup>6</sup> Muspratt, *ibid.*, 1860, 50, 259.

<sup>7</sup> Remelé, *Pogg. Annalen*, 1865, 125, 238.

<sup>8</sup> Girard, *Compt. rend.*, 1852, 34, 22.

<sup>9</sup> Ley, *Ber.*, 1900, 33, 2658; Bruner, *Zeitsch. Chem. Phys. Math.*, 1900, 32, 133.

**Complex Uranyl Sulphites.**—By the addition of potassium bisulphite to a solution of uranyl sulphite in excess of aqueous sulphurous acid, a yellowish-green precipitate of composition  $K_2O \cdot 2UO_3 \cdot 3SO_2$  is obtained.<sup>1</sup> If the uranyl sulphite is treated with a limited quantity of sulphurous acid, golden-yellow crystals separate, which, according to Kohlschütter, may be formulated  $4UO_3 \cdot 4SO_2 \cdot 11H_2O$ , whilst the potassium uranyl salt when treated in the same way yields the compound  $K_2O \cdot 4UO_3 \cdot 5SO_2$ . This, on treatment with water, yields uranyl sulphite and the complex sulphite  $K_2O \cdot 3UO_3 \cdot 2SO_2$ . The latter compound may also be obtained as fine, deep yellow, crystalline needles by treating a solution of uranyl nitrate with an excess of a neutral solution of potassium sulphite.

Corresponding sodium and ammonium salts of the above complexes have been prepared.

Ammonium and potassium salts of composition  $R_2O \cdot UO_3 \cdot 2SO_2$  have also been described.<sup>2</sup>

A basic uranyl sulphite,  $5(UO_2)_2SO_3 \cdot UO_2(OH)_2 \cdot 10H_2O$ , has been described,<sup>3</sup> but that this is a definite compound may be questioned.

**Uranium Sulphate,  $U(SO_4)_2 \cdot nH_2O$ .**—The anhydrous uranous sulphate has not been prepared, but an extraordinarily large number of hydrates is known. Salts containing 1, 2, 3, 4, 5, 6, 7, 8, and 9 molecules of water have been described,<sup>4</sup> and of these the di-, tetra-, octa-, and nona-hydrates are stable. The actual relation of these hydrates to one another is difficult to determine, as they undergo hydrolysis to a considerable extent when in solution, and the tetra- and octa-hydrates, at least, show a marked tendency to remain in a metastable condition at temperatures far removed from the transition-point between the two phases. Solubility determinations indicate that this transition-point is in the neighbourhood of 20° C., but it has been shown that the octahydrate when heated in absence of air changes into the tetrahydrate<sup>5</sup> at 68° to 87° C. when the former hydrate is in a state of metastable equilibrium.

The solubility data on p. 317 have been obtained,<sup>6</sup> but not without difficulty owing to the gradual formation of insoluble basic sulphate<sup>7</sup> and consequent clouding of the solution.

Fig. 7 shows the relation between the two phases.

The tetra-, octa-, and nona-hydrates are isomorphous with the corresponding hydrates of thorium sulphate,<sup>8</sup> and the relation between the uranium salts is probably similar to that between the sulphates of thorium, which are not so subject to hydrolysis and do not remain in the metastable condition to any extent.<sup>9</sup>

<sup>1</sup> Compare Scheller, *Annalen*, 1867, 144, 238.

<sup>2</sup> Kohlschütter, *loc. cit.* See also *Annalen*, 1900, 311, 1.

<sup>3</sup> Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 79.

<sup>4</sup> Orloff, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 381; O. de Coninck, *Bull. Acad. roy. Belg.*, 1901, p. 483; Kohlschütter, *Ber.*, 1901, 34, 3628; Giolitti and Bucci, *Gazzetta*, 1905, 35, ii, 151, 162; Giolitti and Liberi, *ibid.*, 1906, 36, ii, 443.

<sup>5</sup> See Giolitti and Bucci, *loc. cit.*

<sup>6</sup> Giolitti and Bucci, *loc. cit.* The approximate value at 11° to 13° C. is given by O. de Coninck, *Bull. Acad. roy. Belg.*, 1902, pp. 94, 161.

<sup>7</sup> Compare Giolitti and Liberi, *loc. cit.*

<sup>8</sup> Rammelsberg, *Zeitsch. Kryst. Min.*, 1889, 15, 640; Hillebrand and Melville, *Amer. Chem. J.*, 1891, 14, 1; *Bull. U.S. Geol. Survey*, No. 90, p. 30, 1892; Wyruboff, *Bull. Soc. franç. Min.*, 1909, 32, 340.

<sup>9</sup> See this series, Vol. V., p. 291.

Temperature, ° C.	Grams $U(SO_4)_2$ per 100 Grams Saturated Solution.	Phase.	Temperature, ° C.	Grams $U(SO_4)_2$ per 100 Grams Saturated Solution.	Phase.
11-13	16.0	$U(SO_4)_2 \cdot 4H_2O$	18	10.17	$U(SO_4)_2 \cdot 8H_2O$
24	9.8	"	25-26	13.32	"
37	8.3	"	37	19.98	"
48.2	8.1	"	48.2	28.72	"
63	7.3	"	67	36.8	"
			93	63.2	"

Uranous sulphate, even in acid solutions, is a strong reducing agent and can precipitate silver and gold from solutions of their salts. The sulphate is readily oxidised in solution by atmospheric oxygen. Both these reactions are accelerated by the presence of catalysts, especially copper salts, and in less degree platinum black or traces of iron salts.<sup>1</sup>

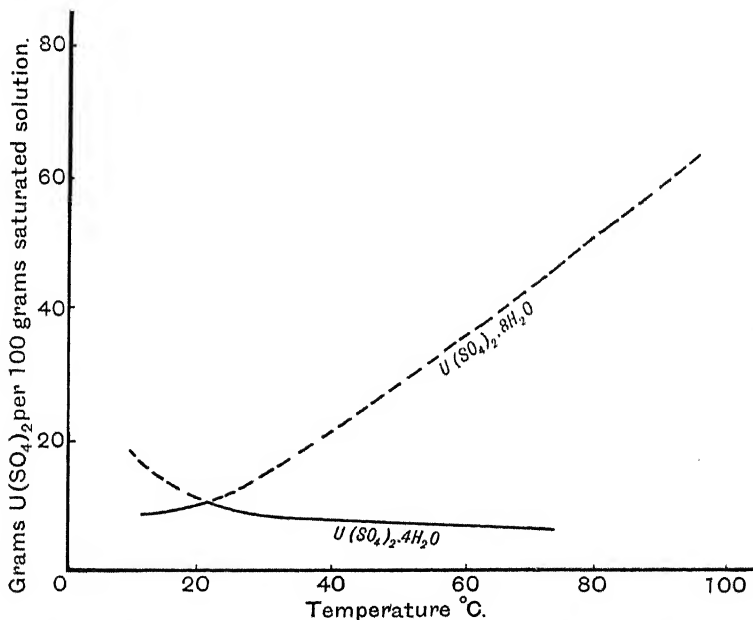


FIG. 7.—Solubility of the tetra- and octa-hydrates of uranous sulphate.

The hydrates are usually prepared by reduction of uranyl sulphate by means of alcohol and exposure to light, or directly from uranous compounds.

The *dihydrate*,  $U(SO_4)_2 \cdot 2H_2O$ , crystallises in grey needles from a solution of uranous oxalate containing concentrated sulphuric acid.<sup>2</sup>

<sup>1</sup> Luther and Michie, *Zeitsch. Elektrochem.*, 1909, 15, 1.

<sup>2</sup> Kohlschütter, *Ber.*, 1901, 34, 3619.

The *tetrahydrate*,  $U(SO_4)_2 \cdot 4H_2O$ , may be prepared by dissolving urano-uranic oxide in concentrated sulphuric acid, adding water, and evaporating the solution *in vacuo*; or by exposing a solution of uranyl sulphate containing alcohol to direct sunlight.<sup>1</sup> Giolitti and Bucci,<sup>2</sup> using the latter method, found that by varying the concentrations of uranyl sulphate and alcohol it was possible to get sometimes the tetrahydrate and sometimes the octahydrate. If sodium hyposulphite is added to a solution of uranyl sulphate until a precipitate begins to form, the addition of alcohol to the solution precipitates a mixture of uranous and uranyl sulphates, from which the latter may be removed by washing with aqueous alcohol. On dissolving the residue in dilute sulphuric acid and evaporating at low temperature, crystals of the tetrahydrate are obtained.<sup>3</sup> A further method consists in triturating uranium oxide with concentrated sulphuric acid and pouring the mixture into alcohol; the precipitate, after washing with alcohol and ether, may be recrystallised from dilute sulphuric acid solution.<sup>4</sup>

The crystals obtained in these preparations are green rhombic bipyramids,<sup>5</sup> stable in the air. They dissolve in water, forming a clear solution, which, however, soon goes turbid owing to the separation of basic sulphate.

The *octahydrate*,  $U(SO_4)_2 \cdot 8H_2O$ , is obtained by exposing to light a solution of uranyl sulphate containing alcohol and sulphuric acid.<sup>6</sup> It may conveniently be prepared<sup>7</sup> by mixing urano-uranic oxide with alcohol and concentrated sulphuric acid, warming gently, and stirring for two or three hours. The product is then dissolved in very dilute sulphuric acid, and the uranous sulphate precipitated by means of alcohol. This is dehydrated at 200° C., the residue dissolved in water, and the solution allowed to crystallise at ordinary temperature over sulphuric acid.

The octahydrate yields small dark green monoclinic prisms, stable in the air. When treated with cold water in large quantity most of it dissolves, about 25 per cent. remaining as a green powdery basic salt,  $UOSO_4 \cdot 2H_2O$ ; <sup>8</sup> with less water the basic salt redissolves and a solution of the normal salt is obtained. The extent to which the sulphate is hydrolysed depends upon the temperature, the solutions being relatively stable between 18° and 105° C. A ten per cent. solution of sulphuric acid dissolves it without hydrolysing it. When heated in absence of air, the octahydrate changes to the tetrahydrate between 68° and 87° C. and becomes anhydrous at 300° C. At the same time it begins to decompose, and at higher temperatures yields uranyl sulphate and finally the green oxide. From an investigation of the rate of dehydration of the octahydrate when kept over sulphuric acid, Giolitti and Bucci formulate the existence of the hydrates:  $U(SO_4)_2 \cdot 7H_2O$ ,  $U(SO_4)_2 \cdot 3H_2O$ , and  $U(SO_4)_2 \cdot 2H_2O$ .

The *nona- or emeca-hydrate*,  $U(SO_4)_2 \cdot 9H_2O$ , is obtained by decomposing a cold solution of uranyl sulphate by means of sodium thio-

<sup>1</sup> Ebelmen, *Ann. Chim. Phys.*, 1842, [3], 5, 190.

<sup>2</sup> Giolitti and Bucci, *Gazzetta*, 1905, 35, n. 151, 162.

<sup>3</sup> Aloy and Auber, *Bull. Soc. chim.*, 1907, [4], 1, 569.

<sup>4</sup> Kohlshütter, *Ber.*, 1901, 34, 3619. See also Giolitti and Bucci, *loc. cit.*

<sup>5</sup> Hillebrand and Melville, *Amer. Chem. J.*, 1891, 14, 1.

<sup>6</sup> Orloff, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 381; Giolitti and Bucci, *loc. cit.*

<sup>7</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1909, 32, 340.

<sup>8</sup> Giolitti and Bucci, *loc. cit.* Cf. O. de Coninck, *Bull. Acad. roy. Belg.*, 1901, p. 483.

sulphate, and dissolving the precipitate in dilute sulphuric acid. After reprecipitation with alcohol, it is redissolved in the least possible quantity of dilute sulphuric acid, and the solution allowed to crystallise over sulphuric acid.<sup>1</sup> It crystallises in green monoclinic prisms isomorphous with the corresponding thorium salt.

$$a : b : c = 0.5970 : 1 : 0.6555, \quad \beta = 97^\circ 49'.^2$$

The salt effloresces, losing one molecule of water. It gradually loses the remainder of its water on heating, and at red heat decomposes, leaving a residue of urano-uranic oxide.

Uranous sulphate forms *double salts* with the sulphates of the alkali metals. The salts,  $K_2U(SO_4)_3 \cdot 2H_2O$  and  $(NH_4)_8U(SO_4)_6 \cdot 3H_2O$ , have been prepared,<sup>3</sup> the former crystallising in glistening green plates, the latter in deep green, glistening pyramids. Both decompose in cold water with separation of basic sulphate.

*Acid uranous sulphates* have been described, e.g.  $U_2(SO_4)_4 \cdot H_2SO_4$ ,<sup>4</sup>  $U(SO_4)_2 \cdot H_2SO_4 \cdot 10H_2O$ ,<sup>5</sup> and  $UH(SO_4)_2$ .<sup>6</sup> The latter, which separates in dark brown leaflets when a solution of uranium trichloride is added to concentrated sulphuric acid at 0° C., may contain trivalent uranium.

**Uranium Dithionates.** By the addition of sodium dithionate to solutions of uranous chloride the following basic salts have been obtained: <sup>7</sup>  $7UO_2 \cdot S_2O_6 \cdot 8H_2O$ ;  $6UO_2 \cdot S_2O_6 \cdot 10H_2O$ ;  $8UO_2 \cdot S_2O_6 \cdot 21H_2O$ .

**Uranyl Sulphate**,  $UO_2SO_4$ , is obtained as amber-yellow non-fluorescent crystals when uranyl hydroxide is dissolved in concentrated sulphuric acid and the solution is evaporated;<sup>8</sup> or when either of its hydrates is heated to 300° C. The *trihydrate*,  $UO_2SO_4 \cdot 3H_2O$ , crystallises from a solution of uranyl hydroxide in dilute sulphuric acid; or it may be obtained by dissolving urano-uranic oxide in concentrated sulphuric acid, diluting the solution, and boiling with nitric acid in order to oxidise the uranous salt present; or by triturating potassium hydrogen sulphate with uranyl hydroxide,<sup>9</sup> taking up with water, and concentrating the solution. It forms yellowish-green prismatic crystals, which under the microscope show a beautiful fluorescence.<sup>10</sup> They have density at 16.5° C. 3.280.<sup>11</sup> In the air the crystals slowly effloresce; on heating they lose more water, and at 115° C. yield the monohydrate. This hydrate, in moist air, takes up water again and reforms the trihydrate.<sup>12</sup>

Uranyl sulphate is readily soluble in water, but accurate solubility determinations have not been made. According to O. de Coninck,<sup>13</sup> the trihydrate dissolves in about twenty times its weight of water at

<sup>1</sup> Wyrnoff, *loc. cit.*; see also Rammelsberg, *Pogg. Annalen*, 1842, 55, 318; 56, 125; 1843, 59, 1; *Ber.*, 1872, 5, 1003.

<sup>2</sup> Rammelsberg, *Ber.*, 1886, 19, 603; *Zeitsch. Kryst. Min.*, 1889, 15, 640.

<sup>3</sup> Kohlschütter, *Ber.*, 1901, 34, 3619; cf. Rammelsberg, *loc. cit.*

<sup>4</sup> Kohlschütter, *loc. cit.*

<sup>5</sup> Giolitti and Bucci, *loc. cit.*

<sup>6</sup> Rosenheim and Loebel, *Zeitsch. anorg. Chem.*, 1908, 57, 234.

<sup>7</sup> Klüss, *Chem. Zentr.*, 1888, p. 215; *Annalen*, 1888, 246, 179, 284.

<sup>8</sup> Schultz-Sellack, *Ber.*, 1871, 4, 13.

<sup>9</sup> O. de Coninck, *Bull. Acad. roy. Belg.*, 1904, p. 833.

<sup>10</sup> Reusch, *Zeitsch. Kryst. Min.*, 1884, 9, 561.

<sup>11</sup> Schmidt; see Abegg-Auerbach, *Handbuch der anorganischen Chemie*, Leipzig, 1921,

IV., 1, ii., p. 942.

<sup>12</sup> Lescaur, *Ann. Chim. Phys.*, 1895, [7], 4, 213, 231.

<sup>13</sup> O. de Coninck, *Bull. Acad. roy. Belg.*, 1901, 23, 349.

ordinary temperature, and the solubility decreases with rise in temperature.<sup>1</sup> The heat of solution at 18° to 20° C. is +5100 calories.<sup>2</sup>

The equivalent conductivities of solutions containing  $\frac{1}{2}\text{UO}_2\text{SO}_4$  in  $v$  litres at 25° C. are as follows :<sup>3</sup>

$v = 4$	8	16	32	64	128	256	512	1024
$\Lambda = 17.1$	20.5	25.5	32.0	41.5	53.2	67.7	85.2	103.4.

The difference between  $\Lambda_{32}$  and  $\Lambda_{1024}$ , 71.4, is, as in the case of uranyl chloride and nitrate, unusually high, probably because dissociation takes place in stages. If the solutions are kept for some time, the conductivity increases owing to the increase in hydrogen ions due to hydrolysis. The migration velocity of the uranyl ion at 25° C. is, according to Dittrich, 56. The conductivities at higher temperatures have been determined<sup>4</sup> as follows (for  $\frac{1}{2}\text{UO}_2\text{SO}_4$  in  $v$  litres) :

	$v = 8$	16	64	256
$\Lambda$ at 35° C.	48.2	61.9	82.9	117.2
$\Lambda$ „ 50° C.	59.1	69.8	98.9	141.3
$\Lambda$ „ 65° C.	70.2	87.0	114.3	162.2

Freezing-point determinations show that uranyl sulphate dissociates in dilute solutions to a much less extent than the chloride or nitrate.

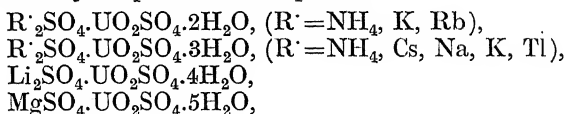
Solutions of uranyl sulphate are fairly stable in diffused daylight, even in presence of alcohol, but readily undergo reduction when placed in direct sunlight or in ultra-violet light (see p. 288).

*Uranyl acid sulphate*,  $\text{UO}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ , is obtained in fine yellow fluorescent crystals when a solution of uranyl sulphate in moderately concentrated sulphuric acid is evaporated at 200° C.<sup>5</sup> It is very deliquescent and readily soluble in water. By evaporating at 60° C. a solution containing uranyl sulphate (1 molecule) and sulphuric acid (5 molecules), similar crystals of composition  $2\text{UO}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$  are obtained.<sup>6</sup>

*Basic uranyl sulphates* of composition  $3\text{U}_2\text{O}_3 \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$  and  $4\text{U}_2\text{O}_3 \cdot \text{SO}_3 \cdot 7\text{H}_2\text{O}$  have been obtained<sup>7</sup> by evaporating at 250° C. solutions of uranyl sulphate containing 3 and 15 per cent. respectively. The former yields citron-yellow, and the latter greyish-yellow, microscopic crystals.

*Ammonio-uranyl Sulphates*.—Uranyl sulphate forms yellow addition compounds with ammonia, of composition  $\text{UO}_2\text{SO}_4 \cdot x\text{NH}_3$ , where  $x=2$ , 3, or 4, the colour of which deepens with increasing ammonia content.<sup>8</sup>

Complex uranyl sulphates, of composition



<sup>1</sup> O. de Coninck has determined the densities of aqueous solutions (1 to 12 per cent.). He also gives (*Bull. Acad. roy. Belg.*, 1901, p. 222; 1902, pp. 94, 161) solubilities in various inorganic and organic solvents.

<sup>2</sup> Aloy, *Compt. rend.*, 1896, 122, 1541.

<sup>3</sup> Dittrich, *Zeitsch. physikal. Chem.*, 1899, 29, 449.

<sup>4</sup> West and Jones, *Amer. Chem. J.*, 1910, 44, 508. See also Winston and Jones, *ibid.*, 1911, 46, 368; Howard and Jones, *ibid.*, 1912, 48, 526.

<sup>5</sup> Schultz-Sellack, *Ber.*, 1871, 4, 13.

<sup>6</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1909, 32, 340.

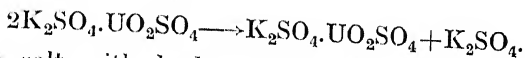
<sup>7</sup> Athanasesco, *Compt. rend.*, 1886, 103, 271.

<sup>8</sup> von Unruh, *Einwirkung von Ammoniak auf Uranylsalze*, Dissertation, Rostock, 1909.

have been described.<sup>1</sup> They are usually obtained from a solution of the diuranate in sulphuric acid, or by crystallisation *in vacuo* of solutions of the mixed salts.

The *potassium salt*,  $K_2SO_4 \cdot UO_2SO_4 \cdot 2H_2O$ , may also be prepared by triturating uranyl hydroxide with potassium hydrogen sulphate, taking up the mixture with water, and evaporating the solution. It was in this salt that Becquerel first discovered radioactivity (see p. 341). It yields yellow fluorescent crystals of density at  $19.1^\circ C. = 3.363$ .<sup>2</sup> The crystals, like those of the corresponding ammonium and rubidium salts, belong to the monoclinic system.<sup>3</sup> The salt is stable towards water. When heated, it becomes anhydrous at  $120^\circ C$ .

The *double salt*,  $2K_2SO_4 \cdot UO_2SO_4$ , is obtained by dissolving uranyl sulphate and excess of potassium sulphate in hot water, and crystallising from the hot solution.<sup>4</sup> At temperatures below  $80^\circ C$ . the salt is decomposed by water thus :



A double salt with hydroxylamine sulphate,<sup>4</sup>  $(NH_2OH)_2H_2SO_4 \cdot 2UO_2SO_4 \cdot 5H_2O$ , and an ethylenediammonium uranyl sulphate,<sup>5</sup>  $C_2H_4(NH_2)_2H_2SO_4 \cdot UO_2SO_4 \cdot 4H_2O$ , have been prepared.

**Uranyl Pyrosulphate**,  $UO_2S_2O_7$ , may be prepared by adding liquid sulphur trioxide to a solution of anhydrous uranyl sulphate in concentrated sulphuric acid.<sup>6</sup> It separates in small, yellow, fluorescent crystals which are very hygroscopic.

**Uranyl Thiosulphate**,  $UO_2S_2O_3$ , appears as a yellow precipitate when sodium thiosulphate is added to a solution of a soluble uranyl salt.<sup>7</sup>

**Uranyl Dithionate** is not stable. When sodium dithionate is added to a solution of a uranyl salt, the yellow solution may be evaporated to the consistency of a syrup, but on further concentration *in vacuo* over sulphuric acid it undergoes decomposition with evolution of sulphur dioxide.<sup>8</sup>

## URANIUM AND SELENIUM.

**Uranium Sesquiselenide**,  $U_2Se_3$ , is formed when a current of hydrogen mixed with a small proportion of selenium vapour is passed rapidly over the double sodium uranium chloride,  $Na_2U_4Cl_{16}$ , at  $1000^\circ C$ .<sup>9</sup>

**Uranium Diselenide**, **Uranous Selenide**,  $USe_2$ , is formed when a current of hydrogen bearing excess of selenium vapour is passed over the double chloride at low red heat ;<sup>9</sup> or by fusing the same chloride

<sup>1</sup> Arfvedson, *Pogg. Annalen*, 1824, **i**, 245; *Schweigger's J.*, 1825, **44**, 8; Berzelius, *Pogg. Annalen*, 1824, **i**, 359; *Schweigger's J.*, 1825, **44**, 191; O. de Coninck, *Bull. Acad. roy. Belg.*, 1904, p. 1171; 1905, pp. 50, 94; O. de Coninck and Chauvenet, *ibid.*, 1905, pp. 151, 182; 1908, p. 50; Rimbach, *Ber.*, 1904, **37**, 461; Kohn, *Zeitsch. anorg. Chem.*, 1908, **59**, 111.

<sup>2</sup> Schmidt; see Abegg-Auerbach, *Handbuch der anorganischen Chemie*, Leipzig, 1921, IV., **i**, ii., 944.

<sup>3</sup> de la Provostaye, *Ann. Chim. Phys.*, 1842, [3], **6**, 165.

<sup>4</sup> Rimbach, *loc. cit.*

<sup>5</sup> Grossmann and Schüek, *Zeitsch. anorg. Chem.*, 1906, **50**, 21.

<sup>6</sup> Schultz-Sellack, *loc. cit.* See also Péligot, *Ann. Chim. Phys.*, 1844, [3], **12**, 549; Drenckmann, *Jahresber.*, 1861, p. 256.

<sup>7</sup> Faktor, *Pharm. Post.*, 1901, **34**, 485; *Chem. Zentr.*, 1901, ii., 878.

<sup>8</sup> Klüss, *Annalen*, 1888, **246**, 179.

<sup>9</sup> Colani, *Compt. rend.*, 1903, **137**, 382; *Ann. Chim. Phys.*, 1907, [8], **12**, 59.



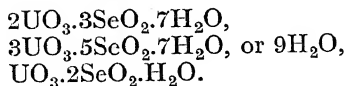
with certain metallic selenides (compare  $\text{US}_2$ , p. 314), preferably stannous selenide. It is obtained in very small black crystals, often pyrophoric. It is readily oxidised, and is vigorously attacked by nitric acid.

**Uranyl Selenide**,  $\text{UO}_2\text{Se}$ , is prepared by heating together selenium (7 parts), potassium cyanide (5 parts), and urano-uranyl oxide (1 part) at a low red heat. It yields black hexagonal prisms with a metallic lustre.<sup>1</sup> It is readily decomposed by acids.

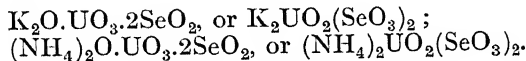
**Uranous Selenate** is unstable<sup>2</sup> and has not been prepared in the pure condition.

**Uranyl Selenite**,  $\text{UO}_2\text{SeO}_3 \cdot 2\text{H}_2\text{O}$ , is obtained as a lemon-yellow precipitate when sodium selenite is added to a solution of a uranyl salt.<sup>3</sup> The anhydrous salt,  $\text{UO}_2\text{SeO}_3$ , is formed by heating the dihydrate with water and a little selenious acid in a sealed tube at  $200^\circ \text{C}$ . It yields microcrystalline needles, which are active towards polarised light. It decomposes on heating, leaving a residue of the green oxide.

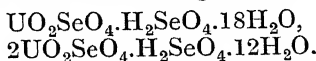
*Complex Uranyl Selenites*.—A series of crystalline compounds, rich in selenious acid, have been prepared<sup>4</sup> by decomposing uranyl salts in solution by means of selenious acid or an alkali selenite. The products are yellow in colour and insoluble in water. Compounds of the following composition have been prepared :



By dissolving an alkali uranate in aqueous selenious acid, and allowing the solution to crystallise, the following compounds have been obtained :



**Uranyl Selenate**,  $\text{UO}_2\text{SeO}_4 \cdot x\text{H}_2\text{O}$ , is present in the glassy mass obtained by evaporating a solution of uranyl hydroxide in selenic acid.<sup>5</sup> It has not been obtained in a pure state. Such solutions also yield acid salts, of which the following have been isolated :



Double selenates, of composition  $\text{R}'_2\text{SeO}_4 \cdot \text{UO}_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{R}' = \text{K}, \text{NH}_4$ ), have been obtained<sup>5</sup> in crusts of yellow crystals by evaporation of solutions of the alkali uranate in selenic acid.

#### URANIUM AND TELLURIUM.

**Uranium Telluride**,  $\text{U}_2\text{Te}_3$ .—This is the only compound of uranium and tellurium the existence of which is definitely established. It is formed when hydrogen containing tellurium vapour is passed over the double sodium uranium chloride at  $1000^\circ \text{C}$ ., or when the chloride is heated with sodium telluride in hydrogen at the same temperature.<sup>6</sup>

<sup>1</sup> Milbauer, *Zeitsch. anorg. Chem.*, 1904, 42, 450.

<sup>2</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1909, 32, 340.

<sup>3</sup> Nilson, *Bull. Soc. chim.*, 1875, 23, 497; *Researches on the Salts of Selenious Acid*,

Upsala, 1875; Boutzoureano, *Ann. Chim. Phys.*, 1889, [6], 18, 341.

<sup>4</sup> Boutzoureano, *loc. cit.*; Sendtner, *Annalen*, 1879, 185, 329.

<sup>5</sup> Sendtner, *loc. cit.*

<sup>6</sup> Colani, *loc. cit.*

The latter method is the more satisfactory. It yields black lustrous crystals.

According to Gutbier,<sup>1</sup> the addition of a uranyl salt to a solution of potassium tellurate yields a yellow curdy precipitate of uranyl tellurate.

Uranyl chromate (see p. 71).

Uranous and uranyl molybdates (see p. 154).

Uranous and uranyl tungstates (see p. 232).

### URANIUM AND NITROGEN.

**Uranium Nitrides.**—It was observed by Moissan<sup>2</sup> that uranium metal combined directly with nitrogen at 1000° C., yielding a yellow nitride the composition of which has not been ascertained. By heating uranous chloride in a stream of dry ammonia,<sup>3</sup> or by heating to redness the double chloride  $\text{Na}_2\text{UCl}_6$  in a current of ammonia,<sup>4</sup> a greyish-black crystalline nitride, of composition  $\text{U}_3\text{N}_4$ , is obtained. It is probable that this compound is frequently present in metallic uranium, for the latter when exposed to kathode rays has been observed<sup>5</sup> to evolve a little nitrogen. It has been suggested<sup>6</sup> that the activity of uranium carbide as a catalyst in the synthesis of ammonia from nitrogen and hydrogen depends on nitride formation.

When uranyl chloride is heated in ammonia a product of uncertain composition, probably an *oxy-nitride*, is obtained.<sup>7</sup>

**Uranous Nitrate** has not been obtained in the solid form. It appears to exist in the unstable green solution obtained on the addition of uranous hydroxide to a neutral solution of silver nitrate (see p. 302). A light green basic nitrate has been obtained by short exposure to light of an alcoholic solution of uranyl nitrate, and rapid filtration of the product.<sup>8</sup>

**Uranyl Nitrate**,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , is the most important compound of uranium; it has received much attention from investigators and is the most widely used uranyl salt of commerce. It is obtained directly from uraninite (see p. 277), and the commercial preparation, which generally contains a small amount of impurity, especially alkali,<sup>9</sup> may be purified by recrystallising several times from water.<sup>10</sup>

It may be prepared by dissolving any of the oxides or hydroxides of uranium in nitric acid and concentrating the solution; or by double decomposition of uranyl chloride with silver nitrate. It crystallises in lemon-yellow prisms, the form of which varies according to the nature of the solvent. The crystals exhibit a yellowish-green fluorescence which does not increase, as is usually the case with phosphorescent substances, even at such a low temperature as  $-190^\circ \text{C}$ .<sup>11</sup> They also

<sup>1</sup> Gutbier, *Zeitsch. anorg. Chem.*, 1902, 31, 340.

<sup>2</sup> Moissan, *Compt. rend.*, 1896, 122, 274.

<sup>3</sup> Uhrlaub, *Verbindungen einiger Metalle mit Stickstoff*, Dissertation, Göttingen, 1861.

See also Kohlshütter, *Annalen*, 1901, 317, 158.

<sup>4</sup> Colani, *Compt. rend.*, 1903, 137, 382.

<sup>5</sup> Jorissen and Trivelli, *Chem. Weekblad*, 1911, 8, 59.

<sup>6</sup> Haber and Greenwood, *Zeitsch. Elektrochem.*, 1915, 21, 241. Compare Haber and

Le Rossignol, *ibid.*, 1913, 19, 68.

<sup>7</sup> Smith and Matthews, *J. Amer. Chem. Soc.*, 1895, 17, 687.

<sup>8</sup> Benrath, *Zeitsch. wiss. Photochem.*, 1917, 16, 253.

<sup>9</sup> Giolitti and Tavanti, *Gazzetta*, 1908, 38, ii., 239.

<sup>10</sup> McCoy and Ashman, *Amer. J. Sci.*, 1908, [4], 26, 521.

<sup>11</sup> J. Becquerel, *Compt. rend.*, 1911, 152, 511.

possess the remarkable properties of triboluminescence, emitting flashes of light when mechanically shaken or crushed, of detonation, or even in some cases of violent explosibility. The phenomena were first described by Ivanov,<sup>1</sup> but subsequent investigators observed that the crystals were only explosive when free nitric acid was present and when they had been obtained by crystallisation from ether.<sup>2</sup> Explosions never occurred with preparations recrystallised from water, although the crystals generally showed triboluminescence. This property appears to diminish with time, but it has been observed in a specimen of the salt which had been kept in a stoppered bottle for forty-one years.<sup>3</sup> Moreover, it does not appear to be connected with the radioactive properties of the salt. If crystallisation is allowed to proceed under the influence of Röntgen rays no effect on the properties of the crystals is observed.<sup>4</sup> A specimen of sodium diuranate, with no triboluminescence, may be converted into a strongly triboluminescent uranyl nitrate.<sup>5</sup> Siemssen<sup>5</sup> suggests that the property is due to electrical tension in the crystals. The less frequently observed explosibility appears to be due to the formation of an unstable compound of the uranyl salt with a lower oxide of nitrogen and ether. According to Andrews<sup>6</sup> some of the water of crystallisation of the hexahydrate is replaced by ether. Eichhorn observed that uranyl nitrate extracted from aqueous solution by means of ether contained less water of crystallisation than the ordinary salt, and explosive specimens of the salt are never obtained when prepared in absence of nitric acid and ether. Two actual compounds of uranyl nitrate with ether have been obtained<sup>7</sup> by drying the ethereal solution over calcium nitrate and cooling to about  $-10^{\circ}$  and  $-70^{\circ}$  C. respectively; when the ether was removed from these compounds by means of a current of dry air, the dihydrate (see below) remained. Analogous compounds, in which the water molecules are replaced by molecules of ammonia, have also been obtained.<sup>8</sup>

The crystals of uranyl nitrate hexahydrate, which have density 2.807 and are diamagnetic,<sup>9</sup> deliquesce in moist air. At  $15^{\circ}$  C. the vapour pressure is practically negligible.<sup>10</sup> The melting-point is  $60.2^{\circ}$  C., and the liquid boils at  $118^{\circ}$  C.<sup>11</sup>

Uranyl nitrate is readily soluble in water, ether, ethyl and methyl alcohols, and other organic solvents. Water at  $18^{\circ}$  C. dissolves twice

<sup>1</sup> Ivanov, *Chem. Zeit.*, 1912, 36, 297.

<sup>2</sup> Andrews, *J. Amer. Chem. Soc.*, 1912, 34, 1686; *Chem. Zeit.*, 1912, 36, 1463; Eichhorn, *Chem. Zeit.*, 1914, 38, 139; Müller, *ibid.*, 1916, 40, 38; 1917, 41, 439.

<sup>3</sup> Siemssen, *Chem. Zeit.*, 1922, 46, 450.

<sup>4</sup> Müller, *loc. cit.*

<sup>5</sup> Siemssen, *Chem. Zeit.*, 1919, 43, 267.

<sup>6</sup> Andrews, *loc. cit.*

<sup>7</sup> Lebeau, *Compt. rend.*, 1911, 152, 439.

<sup>8</sup> von Unruh, *Einwirkung von Ammoniak auf Uranylsalze*, Dissertation, Rostock, 1909.

<sup>9</sup> Moissan, *Traité de Chimie Minérale*, 1905, iv., 879.

<sup>10</sup> Lescœur, *Ann. Chim. Phys.*, 1896, [7], 7, 416.

<sup>11</sup> This salt has also been studied by Haberle, *Gehlen's Allg. J. Chem.*, 1834, 4, 146; de la Provostaye, *Ann. Chim. Phys.*, 1842, [3], 5, 48; Rammelsberg, *Neue Forschungen*, 1842, p. 58; Schabus, *Jahresber.*, 1850, p. 320; O. de Coninck, *Compt. rend.*, 1900, 131, 1219, 1303; 1901, 133, 90, 204; *Bull. Acad. roy. Belg.*, 1901, p. 222; 1909, p. 743; Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 570; de Forcrand, *Compt. rend.*, 1913, 156, 1207.

its weight of the salt.<sup>1</sup> The density of the saturated solution at 17° C. is 1.7536, and its refractive index,  $n_D^{17}$ , = 1.41155.<sup>2</sup>

The equivalent conductivities of solutions containing  $\frac{1}{2}\text{UO}_2(\text{NO}_3)_2$  in  $v$  litres at 25° C. are as follows :<sup>3</sup>

$v$	32	64	128	256	512	1024	2048	4096	$\Lambda_{1024} - \Lambda_{32}$
$\Lambda$ (i)	100.5	107.4	111.7	122.6	130.8	140.2	150.0	161.8	39.7
$\Lambda$ (ii)	103.9		117.8		131.3	139.5	—	—	35.6
$\Lambda$ (iii)		110.8		120.0	128.6	136.1	146.3	—	—

As in the case of the sulphate (see p. 320), the difference  $\Lambda_{1024} - \Lambda_{32}$  is abnormally high for a normal salt of a divalent anion, apparently owing to hydrolysis; the solution has an acid reaction. Dittrich has shown the presence of hydrogen ions in solution by the inversion of sugar, and by cryoscopic measurements has determined the degree of dissociation  $\alpha$  and the molecular weight of the solute at varying dilutions; thus for solutions containing the molecular weight  $(\text{UO}_2(\text{NO}_3)_2 = 394.2)$  in  $v$  litres :

$v$	1	2	4	8	16
$\alpha$	0.78	0.80	0.82	0.88	0.94
Mol. wt.	153.4	151.6	148.9	142.5	137.8

It may be shown by extrapolation<sup>4</sup> that the apparent molecular weight at infinite dilution is almost exactly one-third the real molecular weight, so that ionisation appears to proceed according to the scheme :



Up to an equivalent dilution of 4096 litres, the values of  $\Lambda$  do not converge to a limit. In concentrated solution the salt is ionised to a considerable extent, and it is doubtful whether it may be considered as a simple ternary electrolyte. The addition of ammonia to the solution precipitates ammonium diuranate, thus indicating the probable presence of the anion  $\text{U}_2\text{O}_7^{--}$ .

The following conductivity measurements have been obtained for solutions containing  $\frac{1}{2}\text{UO}_2(\text{NO}_3)_2$  in  $v$  litres at 50° C. :<sup>5</sup>

$v$	4	16	64	256	512	1024	2048
$\Lambda$ (1)	134.3	159.3	189.5	211.6	—	246.3	—
$\Lambda$ (2)	121.1	149.3	174.8	201.5	216.4	226.1	250.0

By the dehydration of the hexahydrate, tri-, di-, and mono-hydrates have been obtained. The anhydrous salt has also been described.

When uranyl nitrate hexahydrate is placed in an enclosed space with sulphuric acid at ordinary temperature and pressure it undergoes dehydration in two stages, yielding after a few days the *trihydrate*,

<sup>1</sup> O. de Coninck, *loc. cit.* Cf. Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 570. See O. de Coninck, *Bull. Soc. chim.*, 1915, [4], 17, 422, for tabulated densities of solutions of uranyl nitrate of various concentrations in water, alcohol, methyl alcohol, acetic acid, nitric acid, sulphuric acid, and hydrobromic acid.

<sup>2</sup> Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1183. The original paper contains densities and refractive indices of aqueous solutions containing from 2.80 to 54.77 per cent. of the anhydrous nitrate.

<sup>3</sup> (i) Dittrich, *Zeitsch. physikal. Chem.*, 1899, 29, 449; (ii) Ley, *ibid.*, 1899, 30, 193; *Ber.*, 1900, 33, 2658; (iii) Winston and Jones, *Amer. Chem. J.*, 1911, 46, 403.

<sup>4</sup> Gómez, *Anal. Fis. Quím.*, 1919, 17, 24.

<sup>5</sup> (1) West and Jones, *Amer. Chem. J.*, 1910, 44, 508; (2) Howard and Jones, *ibid.*, 1912, 48, 526.

$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and after about a month the *dihydrate*,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .<sup>1</sup> Reduction of pressure or increase of temperature only accelerates the change. The trihydrate may also be prepared by drying the hexahydrate over lime in a vacuum;<sup>2</sup> by evaporation of a neutral solution of the nitrate at  $65^\circ \text{C}$ .; <sup>3</sup> or by evaporation of an acid solution *in vacuo*.<sup>4</sup> It yields monoclinic crystals which melt at  $121.5^\circ \text{C}$ .<sup>5</sup>

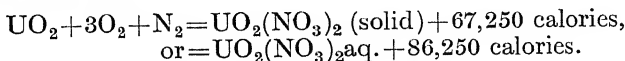
The dihydrate is formed by evaporation at ordinary temperature of an ethereal solution of the hexahydrate which has been dried with calcium nitrate;<sup>2</sup> or by crystallisation of the hexahydrate from concentrated nitric acid solution.<sup>5</sup> It yields small lustrous plates, thick and square, probably rhombic, and possessing a green fluorescence. It melts at  $179.3^\circ \text{C}$ . It is much more stable than the trihydrate, and can be kept in a vacuum desiccator with caustic alkali or phosphorus pentoxide without any loss of water.<sup>6</sup> It dissolves readily in ether. If the dihydrate is heated in a current of carbon dioxide at  $98^\circ \text{C}$ . a product corresponding very nearly in composition to the *monohydrate*,  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , is obtained;<sup>7</sup> at  $160^\circ \text{C}$ . under the same conditions the *anhydrous salt*,  $\text{UO}_2(\text{NO}_3)_2$ , is obtained. The latter may also be obtained by passing a current of dry nitric anhydride over the trihydrate carefully heated at  $170^\circ$  to  $180^\circ \text{C}$ .<sup>8</sup> It is a yellow amorphous powder, readily soluble in water with evolution of heat. It reacts violently with ether. When heated to  $200^\circ \text{C}$ . it decomposes and leaves a mixture of uranic acid,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ , and uranic anhydride.<sup>6</sup>

By an investigation of the cooling and heating curves for solutions of uranyl nitrate, indications have been obtained<sup>9</sup> of the existence of an icositetra-hydrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ .

The following values for the heats of solution of anhydrous uranyl nitrate and its hydrates have been obtained:

	de Forcrand. <sup>10</sup>	Markétos. <sup>11</sup>
$\text{UO}_2(\text{NO}_3)_2$ . .	+19,000 calories	+16,000 calories
$\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ . .	+11,870 "	
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ . .	+ 5,050 "	+ 5,420 "
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . .	+ 1,350 "	+ 2,000 "
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . .	- 5,450 "	- 4,760 "

The following values for the heat of formation of uranyl nitrate are due to de Forcrand:



<sup>1</sup> de Forcrand, *Compt. rend.*, 1913, 156, 1044; Lebeau, *Bull. Soc. chim.*, 1911, [4], 9, 298; Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 570. Cf. Markétos, *Compt. rend.*, 1912, 155, 210.

<sup>2</sup> Lebeau, *loc. cit.*

<sup>3</sup> Wyruboff, *Bull. Soc. franç. Min.*, 1909, 32, 340.

<sup>4</sup> Schultz-Sellack, *Zeitsch. Chem.*, 1870, [2], 6, 646; Vasilieff, *loc. cit.* Cf. Ditte, *Ann. Chim. Phys.*, 1879, [5], 18, 337; Drenckmann, *Zeitsch. ges. Naturw.*, 1861, 17, 134.

<sup>5</sup> Vasilieff, *loc. cit.*

<sup>6</sup> Lebeau, *Compt. rend.*, 1911, 152, 439; 1912, 155, 163.

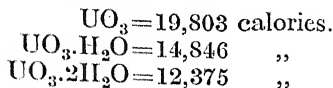
<sup>7</sup> de Forcrand, *loc. cit.*

<sup>9</sup> Germann, *J. Amer. Chem. Soc.*, 1922, 44, 1466.

<sup>10</sup> de Forcrand, *Compt. rend.*, 1913, 156, 1207, 1954; *Ann. Chim.*, 1915, [9], 3, 5.

<sup>11</sup> Markétos, *Compt. rend.*, 1912, 155, 210.

The heats of solution in dilute nitric acid of



By dissolving the dihydrate of uranyl nitrate in fuming nitric acid and treating the cooled solution with a mixture of nitric anhydride and excess of nitrogen peroxide, a light yellow precipitate, of composition  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ , is obtained.<sup>1</sup> It is decomposed by water with liberation of nitrogen peroxide. At 163° to 165° C. it yields the anhydrous uranyl nitrate.

Uranyl nitrate forms double salts of the type  $\text{R} \cdot \text{UO}_2(\text{NO}_3)_3$ , where R = K, NH<sub>4</sub>, Rb, Cs, or Tl. They may be prepared by crystallising a solution of the mixed nitrates in concentrated nitric acid;<sup>2</sup> or by crystallisation from a solution of the alkali uranate in excess of nitric acid.<sup>3</sup> The crystals are all anhydrous, and in the case of the potassium salt are orthorhombic, whilst the rubidium and caesium salts are rhombohedral and isomorphous with each other.<sup>4</sup> The *ammonium* salt yields both orthorhombic and rhombohedral crystals. All exhibit a yellowish-green fluorescence; they are hygroscopic and readily decomposed by water into their components. The *thallium* salt is particularly unstable, being decomposed in moist air. On the other hand, the *rubidium* salt dissolves in water at 80° C. without decomposition.<sup>3</sup> The corresponding salts of sodium, lithium, or of divalent metals have not been prepared.

The following unstable complex nitrates have been obtained:<sup>5</sup>

*Cadmium uranyl nitrate*,  $\text{CdUO}_2(\text{NO}_3)_4 \cdot 30\text{H}_2\text{O}$ , yellow needles, which lose  $10\text{H}_2\text{O}$  when dried *in vacuo* over sulphuric acid;

*Nickel uranyl nitrate*,  $3\text{UO}_2(\text{NO}_3)_2 \cdot 10\text{Ni}(\text{NO}_3)_2$ , greenish-yellow needles; and

*Rhodium uranyl nitrate*,  $\text{RhUO}_2(\text{NO}_3)_5 \cdot 10\text{H}_2\text{O}$ , orange leaflets, which lose  $5\text{H}_2\text{O}$  *in vacuo*.<sup>6</sup>

*Ethylenediammonium uranyl nitrate*,  $\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot 2\text{HNO}_3 \cdot \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , has been prepared.<sup>7</sup>

## URANIUM AND PHOSPHORUS.

**Uranium Monophosphide, UP.**<sup>8</sup>—Uranyl hypophosphite on strongly heating leaves a residue consisting of a mixture of uranous pyrophosphate, uranous metaphosphate, and uranium monophosphide, hydrogen alone escaping.

**Uranous Phosphide, U<sub>3</sub>P<sub>4</sub>.** is obtained in the form of a black microcrystalline powder by fusing together sodium uranous chloride and aluminium phosphide at 1000° C. in a stream of hydrogen;<sup>9</sup> or

<sup>1</sup> Spath, *Monatsh.*, 1912, 33, 853.

<sup>2</sup> Meyer and Wendel, *Ber.*, 1903, 36, 4055.

<sup>3</sup> Rimbach, *ibid.*, 1904, 37, 461.

<sup>4</sup> Sachs, *Zeitsch. Kryst. Min.*, 1903, 38, 496.

<sup>5</sup> Lancelotti, *Chem. Zentr.*, 1912, i, 208.

<sup>6</sup> An impure silver uranyl nitrate has been described by O. de Coninck, *Bull. Acad. Belg.*, 1909, p. 744.

<sup>7</sup> Grossmann and Schück, *Zeitsch. anorg. Chem.*, 1906, 50, 21. For compounds of uranium with hydrazine, see Salvadori, *Atti R. Accad. Lincei*, 1912, [5], 21, ii, 455.

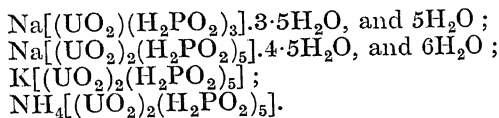
<sup>8</sup> Rammelsberg, *Ber.*, 1872, 5, 492.

<sup>9</sup> Colani, *Compt. rend.*, 1903, 137, 382; *Ann. Chim. Phys.*, 1907, [8], 12, 59.

by the aluminothermic process, using a mixture containing phosphorus and uranyl pyrophosphate or a higher oxide of uranium. Both processes yield a product contaminated with aluminium, which is difficult to remove. A purer crystalline product is obtained by the action of phosphine on sodium uranous chloride, but in this case the yield is poor. The phosphide is slowly oxidised in air to yellow uranyl phosphate. It is slowly decomposed by water, rapidly by nitric acid.

**Uranyl Hypophosphite**,  $\text{UO}_2(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ , is obtained as a yellow crystalline powder when freshly precipitated ammonium diuranate is digested with aqueous hypophosphorous acid.<sup>1</sup> It is insoluble in water, soluble in acids. On heating, it loses water between  $100^\circ$  and  $200^\circ \text{C.}$ , and at higher temperatures decomposes with explosive violence, yielding hydrogen and a residue containing the monophosphide as described above. The *anhydrous* salt,  $\text{UO}_2(\text{H}_2\text{PO}_2)_2$ , may be prepared by agitating solutions of 1 molecular proportion of uranyl nitrate and 4 molecular proportions of sodium hypophosphite.<sup>2</sup> It separates in yellow microcrystalline prisms, insoluble in water, but readily soluble in excess of either reagent. A pale yellow trihydrate has also been obtained.

By the action of alkali hypophosphites on uranyl hypophosphites the following complex salts have been prepared : <sup>2</sup>



**Uranyl Phosphite**,  $(\text{UO}_2)_3\text{H}_6(\text{PO}_3)_4 \cdot 12\text{H}_2\text{O}$ , is precipitated on the addition of ammonium diuranate to an aqueous solution of phosphorus trichloride.<sup>3</sup> On drying in the air it becomes hard and transparent; over sulphuric acid it loses 7 molecules of water. On heating, it loses two-thirds of its water at  $180^\circ \text{C.}$ , and becomes anhydrous, at the same time turning green, at  $300^\circ \text{C.}$

**Uranous Phosphates**.—*Uranous orthophosphate*,  $\text{U}_3(\text{PO}_4)_4$ , is prepared<sup>4</sup> by adding trisodium phosphate to a solution of uranous chloride in an atmosphere of carbon dioxide. It separates as an amorphous precipitate, which, when heated to redness in a current of hydrogen chloride, changes to a green microcrystalline powder. A *basic* phosphate, of composition  $\text{U}_2\text{O}(\text{PO}_4)_2$  or  $2\text{UO}_2 \cdot \text{P}_2\text{O}_5$ , is obtained as a bright green powder when uranyl ortho- or pyro-phosphate is reduced by heating in hydrogen; it becomes crystalline when ignited in hydrogen chloride. The same compound may be obtained<sup>5</sup> by precipitating a solution of uranous chloride by means of excess of trisodium phosphate or sodium pyrophosphate. A *chlorophosphate*,  $\text{UClPO}_4$  or  $3\text{UO}_2 \cdot \text{UCl}_4 \cdot 2\text{P}_2\text{O}_5$ , is obtained by passing the vapour of uranous chloride over heated metaphosphoric acid, or any one of the uranous phosphates, after displacement of the air by carbon dioxide.<sup>6</sup> It yields green orthorhombic crystals,

$$a : b : c = 0.8376 : 1 : 0.7473.$$

<sup>1</sup> Rammelsberg, *Ber.*, 1872, 5, 492.    <sup>2</sup> Rosenheim and Trewendt, *Ber.*, 1922, 55, B, 1957.

<sup>3</sup> Rammelsberg, *Pogg. Annalen*, 1867, 132, 500.

<sup>4</sup> Colani, *Ann. Chim. Phys.*, 1907, [8], 12, 59. See also Werther, *J. prakt. Chem.*, 1848, 43, 321.

<sup>5</sup> Chastaing, *Bull. Soc. chim.*, 1880, [2], 34, 20.

<sup>6</sup> Colani, *loc. cit.*

An *acid* uranium phosphate,  $\text{UH}_2(\text{PO}_4)_2$  or  $\text{UO}_2 \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , is obtained as a gelatinous precipitate when ordinary sodium phosphate,<sup>1</sup> or excess of sodium metaphosphate,<sup>2</sup> is added to a solution of uranous chloride. It may be obtained in the crystalline form as  $\text{UH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ .<sup>3</sup> Aloy<sup>4</sup> also describes a uranous chlorophosphate of composition  $\text{UH}_2(\text{PO}_4)_2 \cdot \text{UCl}_4$  (see p. 295).

*Uranous metaphosphate*,  $\text{U}(\text{PO}_3)_4$ , is prepared by heating to redness a mixture of uranous oxide and metaphosphoric acid; the operation should be carried out in a gold Rose crucible through which carbon dioxide is passed.<sup>5</sup> After washing the product with water and boiling nitric acid, green crystals of the metaphosphate remain. The same compound is obtained when uranium orthophosphate is fused with four times its weight of metaphosphoric acid;<sup>6</sup> or when anhydrous uranyl sulphate is dissolved in metaphosphoric acid at  $316^\circ \text{C}$ .<sup>7</sup> Uranous metaphosphate yields emerald-green rhombic crystals, isomorphous with the corresponding thorium salt<sup>8</sup> and of density 3.9 at  $0^\circ \text{C}$ . It is only slowly attacked by acids, but fused alkalis or alkali chlorides decompose it. When heated strongly, it melts, loses phosphorus pentoxide, and yields the pyrophosphate.

*Uranous pyrophosphate*,  $\text{UP}_2\text{O}_7$ , may be obtained by heating uranous hydrogen phosphate,  $\text{UH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ , in a current of carbon dioxide; or more readily, by calcining the uranyl salt,  $\text{UO}_2\text{H}_4(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , in an atmosphere of hydrogen.<sup>5</sup> The product is amorphous but becomes crystalline without change in composition on heating in a stream of hydrogen chloride. The crystalline form may also be obtained by passing the vapour of phosphorus oxychloride over urano-uranic oxide. The crystals are not well defined and are almost colourless. The *trihydrate*,  $\text{UP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , is formed according to Rammelsberg<sup>9</sup> as a gelatinous precipitate by the addition of sodium pyrophosphate to a solution of uranous chloride.

Complex phosphates of uranium and the alkali or alkaline earth metals have been prepared<sup>5</sup> by fusing an intimate mixture of the alkali phosphate with an excess of uranous oxide in a platinum Rose crucible through which carbon dioxide was passing. The fusion may be facilitated by the addition of a little alkali chloride. On slowly cooling the crucible, well-defined crystals of the double phosphate are formed. If the alkali metaphosphate is used, salts of the type  $\text{R}_2\text{U}(\text{PO}_4)_2$  where  $\text{R} = \text{K}, \text{Na}$ ;  $\text{R}_2 = \text{Ca}, \text{Sr}, \text{Ba}$ , are obtained.

The *potassium* salt,  $\text{K}_2\text{U}(\text{PO}_4)_2$ , forms green, orthorhombic crystals,

$$a : b : c = 0.3711 : 1 : 0.3902,$$

and is soluble in concentrated acids.

The *sodium* salt,  $\text{Na}_2\text{U}(\text{PO}_4)_2$ , is better prepared from the pyro-

<sup>1</sup> Rammelsberg, *Pogg. Annalen*, 1842, 55, 318; 56, 125; 1843, 59, 1; *Ber.*, 1872, 5, 1003.

<sup>2</sup> Chastaing, *loc. cit.*

<sup>3</sup> Aloy, *Recherches sur l'uranium et ses composés*, Thesis 21, Paris, 1901, p. 14.

<sup>4</sup> Aloy, *Ann. Chim. Phys.*, 1901, [7], 24, 412.

<sup>5</sup> Colani, *loc. cit.*

<sup>6</sup> Hautefeuille and Margottet, *Compt. rend.*, 1883, 96, 849; see Colani, *loc. cit.*

<sup>7</sup> Johnson, *Ber.* 1889, 22, 976; see Colani, *loc. cit.*

<sup>8</sup> Troost, *Compt. rend.*, 1885, 101, 210.

<sup>9</sup> Rammelsberg, *Jahresber.*, 1872, p. 208.



phosphate, using excess of sodium chloride. It forms emerald-green, orthorhombic crystals,

$$a : b : c = 0.6766 : 1 : 0.4006,$$

and is readily attacked by acids.

The *calcium* salt,  $\text{CaU}(\text{PO}_4)_2$ , forms green monoclinic crystals,

$$a : b : c = 1.508 : 1 : 1.124; \gamma = 93^\circ 29'.$$

The *barium* salt,  $\text{BaU}(\text{PO}_4)_2$ , forms thin green hexagonal plates.

The *strontium* salt,  $\text{SrU}(\text{PO}_4)_2$ , forms orthorhombic crystals,

$$a : b : c = 1.474 : 1 : 1.165.$$

By using the alkali pyrophosphates, the potassium and sodium salts of the type  $\text{R}_{12}\text{U}_3(\text{PO}_4)_8$ , or  $6\text{R}_2\text{O} \cdot 3\text{UO}_2 \cdot 4\text{P}_2\text{O}_5$ , are obtained.

The salt,  $\text{KU}_2(\text{PO}_4)_3$  or  $\text{K}_2\text{O} \cdot 4\text{UO}_2 \cdot 3\text{P}_2\text{O}_5$ , is obtained by heating the orthophosphate,  $\text{K}_2\text{HPO}_4$ , with a slight excess of potassium uranium chloride; it forms small dark green crystals. The corresponding sodium salt is prepared by fusion of sodium metaphosphate with excess of uranous oxide.

**Uranyl Phosphates.**—Well-defined ortho- and pyro-phosphates exist, but little is known of uranyl metaphosphate. Several complex uranyl phosphates have been described.

**Uranyl Orthophosphates.**—The normal salt,  $(\text{UO}_2)_3(\text{PO}_4)_2$ , is formed, according to Werther,<sup>1</sup> as a yellow precipitate when a solution of the normal sodium phosphate is poured into a neutral solution of uranyl nitrate. Uranyl monohydrogen phosphate,  $\text{UO}_2\text{HPO}_4$ , is obtained as a yellow amorphous precipitate by adding phosphoric acid, or a soluble phosphate,<sup>2</sup> to a solution of uranyl acetate or nitrate; or by treating uranyl hydroxide with phosphoric acid. If the precipitate is boiled for some considerable time with dilute hydrochloric acid, it becomes converted into tetragonal crystals of composition  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ . A *trihydrate*,  $\text{UO}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ , is also obtained<sup>3</sup> by the addition of sodium dihydrogen phosphate on an acid solution of uranyl nitrate; it separates as a sulphur-yellow crystalline powder. The *ammonium* salt,  $\text{UO}_2(\text{NH}_4\text{PO}_4) \cdot \text{H}_2\text{O}$ , is formed when a soluble phosphate is added to a solution containing an ammonium and a uranyl salt. The greenish-yellow precipitate is quite insoluble in presence of acetic acid or ammonium acetate, so that the precipitation is quantitative, and is therefore employed in the volumetric estimation of phosphates (see also p. 338), with potassium ferrocyanide or cochineal as indicator.<sup>4</sup> Upon ignition the precipitate is converted to uranyl pyrophosphate,  $(\text{UO}_2)_2\text{P}_2\text{O}_7$ .

By cooling a hot concentrated solution of uranyl monohydrogen phosphate in nitric acid, a *phosphonitrate* of composition<sup>5</sup>  $\text{UO}_2\text{HPO}_4 \cdot \text{HNO}_3 \cdot 7\text{H}_2\text{O}$ , or  $2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{N}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$ , separates. This is decomposed by water with separation of nitric acid.

<sup>1</sup> Werther, *J. prakt. Chem.*, 1848, 43, 321.

<sup>2</sup> Bourgeois, *Bull. Soc. chim.*, 1897, 19, 733; Debray, *Ann. Chim. Phys.*, 1861, [5], 61, 419. Cf. Heintz, *Annalen*, 1869, 151, 216; Werther, *loc. cit.*

<sup>3</sup> Werther, *loc. cit.*; Lienau, *Dissertation*, Berlin, 1898.

<sup>4</sup> Pineus, *J. prakt. Chem.*, 1839, 76, 104; *Jahresber.*, 1859, p. 667; Leconte, *Compt. rend.*, 1849, 29, 55; Girard, *ibid.*, 1852, 34, 22; Sutton, *Chem. News*, 1860, 1, 97, 122; Büdeker, *Annalen*, 1860, 117, 195; Fresenius, *Jahresber.*, 1871, p. 897; Marcker, *Zeitsch. anal. Chem.*, 1873, 12, 239; Kitchin, *Chem. News*, 1875, 27, 199; Starkenstein, *Biochem. Zeitsch.*, 1911, 32, 235.

<sup>5</sup> Heintz, *loc. cit.*

*Uranyl dihydrogen phosphate*,  $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , is obtained<sup>1</sup> by concentrating a solution of uranic oxide in hot dilute phosphoric acid; it separates in small yellow crystals.

*Uranyl metaphosphate*,  $\text{UO}_2(\text{PO}_3)_2$ , is obtained, according to Rammelsberg,<sup>2</sup> by heating the yellowish-green precipitate produced by the action of nitric acid on uranyl hypophosphite.

*Uranyl pyrophosphate*,  $(\text{UO}_2)_2\text{P}_2\text{O}_7$ , is formed as a precipitate when a solution of sodium metaphosphate is poured into a hot solution of uranyl nitrate. The *tetrahydrate*,  $(\text{UO}_2)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ , is precipitated in yellow microcrystals by double decomposition of sodium pyrophosphate and uranyl nitrate. The hydrate loses water and yields the anhydrous salt at  $120^\circ \text{C}$ .<sup>3</sup> Uranyl pyrophosphate is insoluble in water, alcohol, or ether; but it dissolves in excess of sodium pyrophosphate solution (see below),<sup>4</sup> and also in dilute nitric acid.

**Complex Uranyl Phosphates.**—The following naturally occurring phosphates have been described (see pp. 273-4):

Autunite,  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ;  
 Uranocircite,  $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ; and  
 Chalcolite,  $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

The last named may be prepared synthetically<sup>1</sup> by boiling a solution of copper acetate with uranyl phosphate and treating the precipitate with acetic acid. Corresponding salts of potassium and ammonium have been prepared. The *potassium salt*,  $\text{KUO}_2\text{PO}_4$ , may be formed by fusing together uranyl hydrogen phosphate,  $\text{UO}_2\text{HPO}_4$ , with potassium sulphate;<sup>5</sup> or by dissolving uranic anhydride in molten potassium pyrophosphate.<sup>6</sup> It is obtained as the trihydrate,  $\text{KUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ , in fluorescent crystals, by the addition of potassium dihydrogen phosphate to an acid solution of uranyl nitrate;<sup>7</sup> the reactants should be in the proportion  $\text{KH}_2\text{PO}_4 : \text{HNO}_3 : \text{UO}_3$ . The crystals are insoluble in water or acetic acid, but dissolve readily in solutions of alkali carbonates. The corresponding ammonium salt,  $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ , is obtained in a similar manner and has similar properties. By fusing together tripotassium phosphate and uranic anhydride the compound  $\text{K}_4\text{UO}_2(\text{PO}_4)_2$  is obtained.

When uranyl pyrophosphate is dissolved in excess of sodium pyrophosphate solution, the freezing-point rises to a maximum corresponding with  $3\text{Na}_4\text{P}_2\text{O}_7 \cdot (\text{UO}_2)_2\text{P}_2\text{O}_7$ , and then descends to a minimum at  $2\text{Na}_4\text{P}_2\text{O}_7 \cdot (\text{UO}_2)_2\text{P}_2\text{O}_7$ . The solution up to this point exhibits none of the characteristic reactions of uranyl salts,<sup>8</sup> so that complex formation has evidently taken place. If the solution is evaporated to dryness, and the resulting gummy residue treated with alcohol, a very soluble hygroscopic powder is obtained, to which Pascal gives the formula  $\text{Na}_8[(\text{UO}_2)_2(\text{P}_2\text{O}_7)_3]6\text{H}_2\text{O}$ . If alcohol is added to a solution of sodium pyrophosphate saturated with uranyl pyrophosphate a yellow insoluble

<sup>1</sup> Werther, *loc. cit.*

<sup>2</sup> Rammelsberg, *Ber. K. Preuss. Akad.*, 1872, p. 447.

<sup>3</sup> Kitchin, *loc. cit.*

<sup>4</sup> Persoz, *Ann. Chim. Phys.*, 1847, [3], 20, 315; Girard, *Compt. rend.*, 1852, 34, 22; Chastaing, *Bull. Soc. chim.*, 1880, [2], 34, 20.

<sup>5</sup> Grandeau, *Ann. Chim. Phys.*, 1886, [6], 8, 223.

<sup>6</sup> Ouvrard, *Compt. rend.*, 1880, 110, 1333.

<sup>7</sup> Lienau, *loc. cit.*

<sup>8</sup> Pascal, *Compt. rend.*, 1913, 157, 932.

powder, of composition  $\text{Na}_2(\text{UO}_2)\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , is formed. The stability of these complexes decreases with rise in temperature, and they cannot therefore be obtained from boiling solutions. The anhydrous salt,  $\text{Na}_2(\text{UO}_2)\text{P}_2\text{O}_7$ , may be obtained by fusing together sodium metaphosphate and uranic anhydride.<sup>1</sup> It yields glistening yellow monoclinic prisms.<sup>2</sup>

**Uranyl Aminophosphates.**—By saturating an aqueous solution of phosphoric acid with an amine, and adding uranyl acetate solution, drop by drop, double phosphates of the type  $\text{B}^*\text{H}_2\text{UO}_2\text{PO}_4$  have been prepared.<sup>3</sup> The following have been obtained:  $\text{CH}_3\text{NH}_2 \cdot \text{H}_2\text{UO}_2\text{PO}_4$ ;  $\text{C}_2\text{H}_5\text{NH}_2 \cdot \text{H}_2\text{UO}_2\text{PO}_4$ ; and  $(\text{CH}_3)_3\text{N} \cdot \text{H}_2\text{UO}_2\text{PO}_4$ . The compounds are precipitated in a pale yellow colloidal condition, and when dried *in vacuo* become horny.

## URANIUM AND ARSENIC.

**Uranous Arsenide**,  $\text{U}_3\text{As}_4$ , may be obtained by methods similar to those employed for the phosphide<sup>4</sup> (see p. 327). When obtained by passing hydrogen over a fused mixture of sodium uranous chloride and sodium arsenide it is a greyish powder which readily burns in the air. It is sometimes obtained in a pyrophoric condition. An aluminium-containing product results when the aluminothermic process, using an oxide of uranium and arsenious oxide, is employed. The purest arsenide is obtained in the crystalline form when a mixture of hydrogen and arsenic vapour is passed over sodium uranium chloride. It is rapidly decomposed by nitric acid.

**Uranyl Metarsenite**,  $\text{UO}_2(\text{AsO}_2)_2$ , results as a yellow precipitate<sup>5</sup> when a solution of sodium metarsenite is added to one of uranyl nitrate. It is insoluble in ammonia, but dissolves readily in acids.

**Uranous Arsenate**,  $\text{UH}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , may be prepared by digesting freshly precipitated uranous hydroxide with cold dilute arsenic acid;<sup>6</sup> or by adding arsenic acid to a solution of the hydroxide in sulphuric acid. It yields pale green needle-shaped crystals, insoluble in water but soluble in excess of arsenic acid. A *tetrahydrate*,  $\text{UH}_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ , is formed as a green precipitate when an alkali arsenate is added to a solution of a uranous salt.<sup>7</sup>

**Uranyl Arsenates.**—The *orthoarsenate*,  $(\text{UO}_2)_3(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}$ , occurs in nature as *trögerite* (see p. 274). It is yellow in colour, but on heating turns reddish brown with loss of water; on cooling, the product again becomes yellow.<sup>8</sup> It breaks down when heated with water, yielding micaceous leaflets. The compound has been produced artificially.<sup>9</sup> *Uranyl hydrogen arsenate*,  $\text{UO}_2\text{HAsO}_4 \cdot 4\text{H}_2\text{O}$ , is obtained<sup>10</sup> as a pale yellow powder by the addition of uranyl acetate to a solution

<sup>1</sup> Ouvrard, *Compt. rend.*, 1880, 110, 1333.

<sup>2</sup> For the action of hydrogen peroxide on this salt, see p. 313.

<sup>3</sup> Barthe, *Compt. rend.*, 1911, 152, 1396; *Kolloid Zeitsch.*, 1912, 11, 246.

<sup>4</sup> Colani, *Compt. rend.*, 1903, 137, 382.

<sup>5</sup> Rammelsberg, *Ber. K. Preuss. Akad.*, 1872, p. 447; Reichardt, *Ber.*, 1894, 27, 1028.

<sup>6</sup> Aloy, *Bull. Soc. chim.*, 1899, [3], 21, 613.

<sup>7</sup> Rammelsberg, *Pogg. Annalen*, 1842, 55, 318; 56, 125.

<sup>8</sup> Winkler, *J. prakt. Chem.*, 1873, [2], 7, 7.

<sup>9</sup> Goldschmidt, *Chem. Zentr.*, 1899, 2, 785.

<sup>10</sup> Werther, *Annalen*, 1848, 68, 313.

of arsenic acid or sodium arsenate. It is insoluble in water and acetic acid.

*Uranyl dihydrogen arsenate*,  $\text{UO}_2(\text{H}_2\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$ , separates in small yellow crystals when a solution of uranyl acetate or nitrate containing an excess of arsenic acid is concentrated.<sup>1</sup> The crystals lose their water of crystallisation at  $150^\circ \text{C}$ .

*Uranyl pyroarsenate*,  $(\text{UO}_2)_2\text{As}_2\text{O}_7$ , remains as a yellow powder when the arsenate,  $\text{UO}_2\text{HAsO}_4 \cdot 4\text{H}_2\text{O}$ , or ammonium uranyl arsenate (see below), is heated.<sup>2</sup>

**Complex Uranyl Arsenates.**—Several double arsenates occur in nature (see p. 274): *zeunerite*,  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ; *uranospinite*,  $\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , corresponding to the phosphates, chalcolite and autunite; and *walpurgite*, a basic bismuth uranyl arsenate. Compounds having the same composition as zeunerite and uranospinite may be formed artificially<sup>3</sup> by mixing a solution of precipitated copper carbonate, or of lime, in excess of arsenic acid with a solution of uranyl acetate or nitrate; on allowing to crystallise, rectangular laminae are obtained. By similar means the ammonium salt,  $\text{NH}_4\text{UO}_2\text{AsO}_4$ , containing 3 and  $5\text{H}_2\text{O}$ , has been prepared.<sup>4</sup> The potassium salt is not easily obtained, since the product resulting from double decomposition between potassium arsenate and a uranyl salt varies in composition with the concentration of the solutions.<sup>5</sup> The salt,  $\text{KUO}_2\text{AsO}_4 \cdot 3 \cdot 5\text{H}_2\text{O}$ , has been obtained,<sup>6</sup> by the prolonged action of arsenic acid on potassium uranate, as a yellow powder, stable towards water.

#### URANIUM AND ANTIMONY.

**Uranous Antimonide**,  $\text{U}_3\text{Sb}_4$ , is not obtained by the ordinary methods used for the arsenide<sup>7</sup> (see p. 332). By fusing a mixture of sodium uranous chloride, antimony, and aluminium Colani obtained a silvery white mass practically free from aluminium. The product resembled the phosphide and arsenide in properties, and produced vivid sparks when projected into the Bunsen flame.

**Uranous Antimonate.**—By the addition of sodium metantimonate to a solution of uranous chloride, a precipitate, apparently uranous metantimonate, is obtained.<sup>8</sup> It is insoluble in acids.

#### URANIUM AND CARBON.

**Uranium Carbide**,  $\text{UC}_2$ , was first prepared by Moissan<sup>9</sup> by heating together urano-uranic oxide (50 parts) and sugar charcoal (6 parts) in the electric furnace. By employing a current of 900 ampères and 50 volts, the reaction was complete in five minutes, and the fused mass on cooling yielded a lustrous, crystalline solid, of density 11.28 at

<sup>1</sup> Werther, *loc. cit.*

<sup>2</sup> Werther, *J. prakt. Chem.*, 1848, 43, 321.

<sup>3</sup> Winkler, *loc. cit.* See also Goldschmidt, *Zeitsch. Kryst. Min.*, 1899, 31, 468.

<sup>4</sup> Lienau, *Dissertation*, Berlin, 1898; Puller, *Chem. Zentr.*, 1871, p. 219.

<sup>5</sup> Werther, *loc. cit.* See Abegg-Auerbach, *Handbuch der anorganischen Chemie*, Leipzig, 1921, IV., 1, ii., 954.

<sup>6</sup> Rimbach, with Bürger and Grewe, *Ber.*, 1904, 37, 461.

<sup>7</sup> Colani, *loc. cit.*

<sup>8</sup> Rammelsberg, *loc. cit.*

<sup>9</sup> Moissan, *Compt. rend.*, 1896, 122, 274; "*Le four électrique*," Paris, 1897, p. 238.

18° C. It may also be obtained <sup>1</sup> by fusing the requisite quantities of uranous oxide and carbon in a Ruff electric vacuum furnace.<sup>2</sup> The formula  $U_2C_3$  was given to the product by Moissan, but by careful analysis and metallographic investigation it has been shown <sup>3</sup> that the composition is correctly expressed by the formula  $UC_2$ . The carbide is harder than quartz, but not so hard as corundum. It is often pyrophoric, and is readily oxidised; it inflames readily on crushing in an agate mortar, and will emit sparks when merely shaken in a strong glass vessel or when two pieces of the carbide are rubbed together. It melts at a temperature somewhat above 2250° C.<sup>4</sup> It is attacked by fluorine at low temperatures, yielding uranous fluoride, but if a little chlorine is also present, the product is uranic fluoride,  $UF_6$ .<sup>1</sup> It reacts with chlorine at 350° C.; with bromine at 390° C.; with iodine below red heat; with nitrogen, yielding nitride, at 1100° C. It burns readily in oxygen at 370° C., forming the green oxide.

Uranium carbide is decomposed by water. The reaction proceeds slowly, and a mixture of solid, liquid, and gaseous hydrocarbons is produced. The gaseous product, which accounts for about one-third of the carbon present,<sup>5</sup> consists of a mixture of the lower paraffin and olefine hydrocarbons, with a little acetylene, and from 30 to 60 per cent. of free hydrogen.<sup>6</sup> The carbide is attacked by dilute mineral acids in the cold; by concentrated acids on warming. Nitric acid decomposes it most readily. Hydrogen chloride and hydrogen sulphide react at about 600° C. Uranium carbide is used as a catalyst in the synthetic production of ammonia.

**Uranous Carbonate** has not been prepared. The addition of an alkali carbonate to uranous chloride solution causes an evolution of carbon dioxide and precipitates an unstable basic carbonate.

**Uranyl Carbonate** occurs in a fairly pure condition in the mineral *rutherfordine* (see p. 273). It has not been obtained artificially. The addition of an alkali carbonate to solutions of uranyl salts yields precipitates of varying composition consisting of basic carbonates sometimes mixed with uranate.<sup>7</sup>

**Complex Uranyl Carbonates.**—A large number of double carbonates exist, usually of the type  $R'_4UO_2(CO_3)_3$ .

**Ammonium Uranyl Carbonate**,  $(NH_4)_4UO_2(CO_3)_3 \cdot 2H_2O$ , is obtained by dissolving freshly precipitated ammonium uranate in a solution of ammonium carbonate at 60° to 70° C.;<sup>8</sup> or by treating a soluble uranyl salt with ammonium carbonate and ammonia.<sup>9</sup> In either case a yellow solution is formed which on evaporation deposits yellow monoclinic crystals of the double carbonate. The same compound results on mixing concentrated solutions of ammonium carbonate (3 molecules) and uranyl nitrate (1 molecule) at 50° to 55° C.,

<sup>1</sup> Ruff and Heinzelmann, *Zeitsch. anorg. Chem.*, 1911, 72, 63.

<sup>2</sup> See Ruff, *Ber.*, 1910, 43, 1564.

<sup>3</sup> Lebeau, *Compt. rend.*, 1911, 152, 955; *Bull. Soc. chim.*, 1911, [4], 9, 512.

<sup>4</sup> Tiede and Birnbrauer, *Zeitsch. anorg. Chem.*, 1914, 87, 129; Ruff and Heinzelmann, *loc. cit.*; Ruff and Goecke, *Zeitsch. angew. Chem.*, 1911, 24, ii, 1459.

<sup>5</sup> Moissan, *loc. cit.*

<sup>6</sup> Lebeau and Damiens, *Compt. rend.*, 1913, 156, 1987.

<sup>7</sup> O. de Coninck, *Bull. Acad. roy. Belg.*, 1904, p. 363; Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 79; Parkmann, *Amer. J. Sci.*, 1862, [2], 34, 326.

<sup>8</sup> Ebelmen, *Ann. Chim. Phys.*, 1842, [3], 5, 189.

<sup>9</sup> Bureker, *J. Pharm. Chim.*, 1878, [4], 27, 347.

and allowing to cool.<sup>1</sup> The crystals have density 2.77.<sup>2</sup> They lose ammonia slowly on keeping; <sup>3</sup> rapidly when heated to 130° C., leaving a residue of uranic anhydride. The carbonate <sup>4</sup> dissolves in water, but the solution decomposes on warming. The solubility at 18.6° C. is <sup>5</sup> 6.04 parts of salt in 100 parts of water. Another ammonium salt,  $(\text{NH}_4)_6(\text{UO}_2)_2(\text{CO}_3)_5 \cdot 4\text{H}_2\text{O}$ , is obtained <sup>1</sup> if ammonium carbonate and uranyl nitrate are mixed in the proportion,  $(\text{NH}_4)_2\text{CO}_3$ , 5 molecules :  $\text{UO}_2(\text{NO}_3)_2$ , 1 molecule. It separates as a yellow crystalline crust.

**Calcium Uranyl Carbonate**,  $\text{CaUO}_2(\text{CO}_3)_2 \cdot 20\text{H}_2\text{O}$ , occurs in nature as *liebigite* (see p. 273). *Voglite* is a similar mineral containing copper. *Uranothallite* is a double carbonate of calcium and uranium,  $\text{Ca}_2\text{U}(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}$  (also see p. 273).

**Potassium Uranyl Carbonate**,  $\text{K}_4\text{UO}_2(\text{CO}_3)_3$ , may be prepared by the action of carbon dioxide on potassium uranyl cyanide,<sup>6</sup> or by evaporating at moderate temperature a solution containing potassium bicarbonate and potassium uranate.<sup>7</sup> It crystallises in small hexagonal prisms, which are stable in dry air and dissolve in cold water without decomposition. The solution is hydrolysed on warming, and the addition of alkali causes precipitation of uranyl hydroxide.

**Sodium Uranyl Carbonate**,  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ , is obtained by evaporation of a solution of freshly precipitated sodium uranate in sodium bicarbonate solution; <sup>7</sup> or by the addition of sodium carbonate in excess to a solution of uranyl acetate.<sup>8</sup> It separates as a yellow crust.

**Thallium Uranyl Carbonate**,  $\text{Tl}_4\text{UO}_2(\text{CO}_3)_3$ , separates as a crystalline precipitate on the addition of thallous nitrate to a solution containing uranium in presence of a carbonate.<sup>9</sup> It is extremely insoluble in water, and the crystals, which are characteristic, may serve for the microchemical detection of uranium.

## URANIUM AND CYANOGEN.

Uranous and uranyl cyanides have not been prepared. The addition of potassium cyanide to solutions of uranous or uranyl salts causes evolution of hydrogen cyanide and precipitation of hydroxide. If, however, an excess of potassium cyanide is added to a solution of a uranyl salt, a clear solution results, which on further addition of the cyanide yields a microcrystalline precipitate of the double cyanide,  $\text{K}_2\text{UO}_2(\text{CN})_4$ .<sup>6</sup> The solution is unstable in the air and gradually releases hydrogen cyanide. The precipitate is also very unstable, and is transformed to a double carbonate by the atmospheric carbon dioxide.

**Potassium Uranyl Ferrocyanide.**—The addition of potassium

<sup>1</sup> Giolitti and Vecchiavelli, *Gazzetta*, 1905, 35, ii., 170.

<sup>2</sup> For crystallographic data, see Keferstein, *Pogg. Annalen*, 1856, 59, 275; de la Provostaye, *Ann. Chim. Phys.*, 1842, [3], 6, 165.

<sup>3</sup> Schlundt and Moore, *Physikal. Zeitsch.*, 1908, 9, 81.

<sup>4</sup> For peroxide derivative of this carbonate, see p. 313.

<sup>5</sup> Ebelmen, *loc. cit.*; *Annalen*, 1842, 43, 286.

<sup>6</sup> Aloy, *Ann. Chim. Phys.*, 1901, [7], 24, 412.

<sup>7</sup> Ebelmen, *loc. cit.*

<sup>8</sup> Anthon, *Dingl. poly. J.*, 1860, 156, 207, 288.

<sup>9</sup> Behrens-Kley, see Abegg-Auerbach, *Handbuch der anorganischen Chemie*, Leipzig, 1921, IV., 1, ii., 955.

ferrocyanide to a solution of uranyl nitrate produces a brown precipitate of a potassium uranyl ferrocyanide, the composition of which, according to Wyruboff,<sup>1</sup> is  $K_3UO_2Fe(CN)_6 \cdot 6H_2O$ ; but according to Atterberg<sup>2</sup> is  $K_6(UO_2)_3[Fe(CN)_6]_4 \cdot 12H_2O$ .

**Uranyl Platinocyanide**<sup>3</sup> is formed by double decomposition between barium platinocyanide and uranyl sulphate. If the solution is crystallised at ordinary temperature, red crystals with strong green metallic reflexion are deposited; but if the solution is evaporated on a water-bath, yellow crystals separate, which turn reddish green on cooling. The latter product changes back to the yellow form at 39° C. The two forms probably represent different degrees of hydration. Unlike most uranyl salts, the platinocyanide does not fluoresce.

**Uranyl Cyanate**,  $UO_2(CNO)_2$ , separates<sup>4</sup> as a golden-yellow powder when alcohol and excess of uranyl nitrate are added to a solution of potassium uranyl cyanate,  $K_2UO_2(CNO)_4$ . The cryoscopic behaviour of solutions of uranyl cyanate containing various proportions of potassium cyanate indicates that the double potassium uranyl salt is present in solutions containing an excess of potassium cyanate. The same complex, which may be formulated  $[UO_2(CNO)_4]K_2$ , is obtained as a voluminous yellow precipitate, possessing a greenish fluorescence, by adding a fresh alcoholic solution of potassium cyanate to a neutral solution of uranyl nitrate. It is very soluble in water, and, owing to hydrolysis, the solution responds to all the tests for uranium, but on keeping, an orange-yellow precipitate of composition  $[(UO_2)_2(CNO)_5]K$  is formed. If, however, an excess of potassium cyanate is present in the solution, a golden-yellow precipitate of composition  $[UO_2(CNO)_3]K$  separates.

**Uranyl Thiocyanate**,  $UO_2(CNS)_2 \cdot 8H_2O$ , may be obtained by the addition of barium thiocyanate to a solution of uranyl sulphate, and evaporation of the resulting red solution in a vacuum over sulphuric acid. It separates in orange-yellow needles, which are very hygroscopic and readily dissolve in water, alcohol, ether, and acetone;<sup>5</sup> ether may be used for extracting it from its aqueous solution. The addition of pyridine to its aqueous solution precipitates a crystalline basic salt of composition  $5UO_2(CNS)_2 \cdot UO_3 \cdot 2H_2O$ .

Double salts of the types  $R_3UO_2(CNS)_5 \cdot 6H_2O$  and  $R_5UO_2(CNS)_7 \cdot 2H_2O$  are formed on the addition of an alkali thiocyanate to a solution of uranyl thiocyanate. On evaporation, the double compound separates in orange-yellow to dark red, very deliquescent, crystals. The alkaline earth metals only form double salts of the type  $R'UO_2(CNS)_4 \cdot 6H_2O$ . None of these double thiocyanates in aqueous solution exhibits the properties of a complex salt. Cryoscopic measurements indicate a complete dissociation into the simple ions.

## URANIUM AND SILICON.

**Uranium Silicide**,  $USi_2$ , is obtained from a mixture of urano-uranic oxide (56 parts), silica (180 parts), aluminium filings and flowers

<sup>1</sup> Wyruboff, *Ann. Chim. Phys.*, 1876, [5], 8, 483; 1886, [6], 8, 340.

<sup>2</sup> Atterberg, *Bull. Soc. chim.*, 1875, 24, 355.

<sup>3</sup> Levy, *Proc. Camb. Phil. Soc.*, 1907, 14, 159.

<sup>4</sup> Pascal, *Compt. rend.*, 1913, 157, 932; *Bull. Soc. chim.*, 1914, [4], 15, 11.

<sup>5</sup> Pascal, *Compt. rend.*, 1914, 158, 1672. Cf. Skey, *Chem. News*, 1867, 16, 201.

of sulphur (each 250 parts), by the aluminothermic method.<sup>1</sup> The product after ignition is treated successively with dilute hydrochloric acid, sodium hydroxide, aqua regia, dilute hydrochloric acid, sodium hydroxide, and finally with water. The silicide remains as lustrous, grey, cubic crystals, of density 8.0. It is stable towards acids, except hydrofluoric acid. It burns slowly in oxygen at 800° C. Chlorine reacts at 500° C., giving a mixture of uranous and silicon chlorides. Fused alkalis oxidise it completely at red heat to uranate and silicate.

**Uranyl Silicate** is formed as a crystalline precipitate when a solution of sodium silicate is added to a 10 per cent. solution of a uranyl salt.<sup>2</sup>

**Hydrated Silicates** of uranium occur in nature as *gummite* and allied minerals (see p. 273); *uranophane* or *uranotil* is a complex calcium uranyl silicate.

A **silicofluoride**<sup>3</sup> of uranium has been described. It is soluble in water and in alcohol.

### URANIUM AND BORON.

**Uranium Boride**,  $UB_2$ , is obtained in silvery-grey fragments by passing an electric arc between electrodes (made by compressing an intimate mixture of powdered metallic uranium and amorphous boron<sup>4</sup>) in a vacuum electric furnace. The boride is stable towards alkalis and acids, except hydrofluoric and nitric acids. It is readily attacked by fused alkali hydroxide.

**Uranyl Borate**.—Uranyl salts are precipitated by the addition of a solution of borax.<sup>5</sup>

**Uranyl Perborate**,  $UBO_4$ , is a yellow, stable compound obtained by the action of a perborate solution on uranium dioxide.<sup>6</sup> Like other perborates, it acts as a strong oxidising agent, and with water or dilute acids it forms hydrogen peroxide.

A complex uranyl borotungstate has been described.<sup>7</sup>

### DETECTION AND ESTIMATION OF URANIUM.

Metallic uranium dissolves readily in hydrochloric or sulphuric acid, but is rather less soluble in nitric acid. It is insoluble in alkaline solutions. The colours of uranium compounds are distinctive, uranous salts being green or blue and forming green or bluish-green solutions, whilst the uranyl salts are yellow. The former act as powerful reducers; the latter are more stable and are in more general use. Both in solution exhibit characteristic absorption spectra.<sup>8</sup>

**Detection in the Dry Way**.—When a uranium compound is heated in a borax bead, or in a bead of microcosmic salt, in an oxidising flame, an orange-yellow coloured bead results which may become greenish on cooling. In the reducing flame the bead assumes a green colour.

**Detection by Reactions in Solution**.—Solutions of uranous salts

<sup>1</sup> Defaeqz, *Compt. rend.*, 1908, 147, 1050; *Bull. Soc. chim.*, 1909, [4], 5, 3.

<sup>2</sup> Bornträger, *Jahresber.*, 1893, p. 401.

<sup>3</sup> Stolba, *Zeitsch. anal. Chem.*, 1864, 3, 72.

<sup>4</sup> Wedekind, *Ber.*, 1913, 46, 1198.

<sup>5</sup> Richter, *Gehlen's J. der Chem.*, 1804, 4, 402.

<sup>6</sup> Bruhat and Dubois, *Compt. rend.*, 1905, 140, 506.

<sup>7</sup> Klein, *Bull. Soc. chim.*, 1881, [2], 36, 207; *Ann. Chim. Phys.*, 1883, [5], 28, 391.

<sup>8</sup> See p. 281. Also Meyer and Greulich, *Physikal. Zeitsch.*, 1921, 22, 583.



are rapidly oxidised in air, especially in sunlight or in ultra-violet light. The addition of alkali precipitates reddish-brown uranous hydroxide, insoluble in excess, but soluble in ammonium carbonate. Solutions of uranyl salts give with alkali hydroxides and carbonates a yellow amorphous precipitate of the alkali diuranate, which dissolves in ammonium carbonate, forming a soluble double carbonate. The following precipitation reactions also reveal the presence of uranyl salts in solution :

1. An alkali phosphate precipitates yellow uranyl hydrogen phosphate,  $\text{UO}_2\text{HPO}_4$ , or in presence of an ammonium salt, uranyl ammonium phosphate,  $\text{UO}_2\text{NH}_4\text{PO}_4$  (see p. 330); uranium may be qualitatively separated from chromium and vanadium by this means.<sup>1</sup>

2. Potassium ferrocyanide produces a brown coloration in very dilute solutions; with more concentrated solutions a brownish-red precipitate of potassium uranyl ferrocyanide results (see p. 335).

3. Ammonium sulphide gives a brown precipitate of uranyl sulphide, which on prolonged heating decomposes with separation of sulphur and hydrated uranous oxide.

Uranyl salts may be reduced in solution to the green uranous condition by means of zinc and dilute acid, or more slowly by means of oxalic acid.

Solutions of uranyl salts are not precipitated by the addition of *cupferron*, the ammonium salt of nitrosophenyl-hydroxylamine, but if first reduced by means of zinc, all the uranium may be precipitated in acid solution by means of this reagent.<sup>2</sup> The precipitate is soluble in chloroform. This reaction affords a means of separating vanadium and uranium by successive precipitation.

The presence of uranium may be detected in ores or slags by adding an excess of zinc to a solution in nitric acid. When the reaction subsides, a yellow deposit, apparently of the hydrated trioxide,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , remains on the zinc.<sup>3</sup> The test is not applicable in presence of hydrochloric or sulphuric acid, and it is not successful in presence of large quantities of iron or vanadium; other metals likely to be present, e.g. Au, Pt, Th, Pb, W, Ti, Cr, Hg, Cu, do not interfere.

For the microchemical detection of uranium, the formation of either thallium uranyl carbonate or sodium uranyl acetate may be employed.

**Gravimetric Estimation.**—Many methods for the quantitative determination of uranium have been described, but the following appear to be the most trustworthy : <sup>4</sup> (1) precipitation with ammonia as ammonium diuranate, and ignition to urano-uranic oxide; (2) precipitation of uranyl ammonium phosphate by means of ammonium phosphate in presence of ammonium acetate, and ignition of the precipitate to uranyl pyrophosphate; and (3) precipitation as uranyl sulphide by means of ammonium sulphide, and ignition to urano-uranic oxide.

In the first process the solution containing the uranyl salt is made slightly acid with hydrochloric or sulphuric acid and treated with a slight excess of ammonium hydroxide (free from carbonate) at the boiling-point. It is best to avoid the use of glass vessels as the

<sup>1</sup> Browning, *J. Amer. Chem. Soc.*, 1921, 43, 114.

<sup>2</sup> Auger, *Compt. rend.*, 1920, 170, 995. See also Angeletti, *Gazzetta*, 1921, 51, i., 285.

<sup>3</sup> Buell, *J. Ind. Eng. Chem.*, 1922, 14, 593.

<sup>4</sup> Pierlé, *ibid.*, 1920, 12, 60; Schwarz, *Helv. Chim. Acta*, 1920, 3, 330.

ammonium uranate tends to carry down silica. The ignition of the precipitate should be carried out in a porcelain crucible allowing access to air, as platinum permits diffusion of gases from the flame which cause slight reduction. It has been considered<sup>1</sup> to be more accurate to ignite the precipitate in a stream of hydrogen and weigh as uranous oxide, but this is not the case, owing to the formation of nitride.<sup>2</sup>

The phosphate method is difficult owing to the fineness of the precipitate,<sup>3</sup> and a complete separation from the alkali metals is almost impossible. After boiling for about fifteen minutes, the precipitate becomes crystalline and is more easily filtered. Precautions must be taken in cooling and weighing the ignited uranyl pyrophosphate since it rapidly absorbs moisture.

Precipitation with ammonium sulphide is best performed at 80° C. in presence of ammonium chloride. Some ammonium uranate is always formed, and complete separation from the alkali metals is only obtained by repeating the precipitation.<sup>4</sup> The results obtained by this method are liable to be high owing to some sulphide being oxidised to sulphate during ignition.<sup>5</sup>

Other methods, such as precipitation with hydrogen peroxide,<sup>6</sup> or precipitation with hydrogen fluoride after reduction to the uranous condition,<sup>7</sup> are less satisfactory.<sup>8</sup>

Uranium minerals may be obtained in solution, in a suitable condition for estimation, by the following process. The ore is dissolved in aqua regia, or, if necessary, fused with alkali bisulphate and extracted with hot hydrochloric acid. After evaporation to dryness, the residue is taken up with dilute hydrochloric acid, and the solution saturated with hydrogen sulphide in order to remove any copper, lead, bismuth, arsenic, antimony, or any other metal yielding an insoluble sulphide. The filtrate is concentrated and treated with ammonium carbonate, which precipitates the carbonates of the alkaline earths, iron, and most of the rare earths. The filtrate is neutralised by hydrochloric acid, evaporated to dryness, and the residue ignited to drive off ammonium salts, and then redissolved in dilute acid. The remaining rare earths, and particularly thorium, are next precipitated by the addition of oxalic acid.<sup>9</sup> The filtrate, which contains the uranium in the uranyl condition, may now be precipitated by any of the methods described above.<sup>10</sup>

<sup>1</sup> Rose, *Zeitsch. anal. Chem.*, 1862, 1, 411; Remelé, *ibid.*, 1865, 4, 371; Zimmermann, *Annalen*, 1879, 199, 15; 1882, 216, 1.

<sup>2</sup> Kern, *J. Amer. Chem. Soc.*, 1901, 23, 685; Schwarz, *loc. cit.* See also Giolitti, *Gazzetta*, 1904, 34, ii., 166; 1905, 35, ii., 145.

<sup>3</sup> Newton and Hughes, *J. Amer. Chem. Soc.*, 1915, 37, 1711.

<sup>4</sup> Schwarz, *loc. cit.* Cf. Schoep and Steinkuhler, *Bull. Soc. chim. Belg.*, 1922, 31, 156.

<sup>5</sup> Pierlé, *loc. cit.*

<sup>6</sup> Wunder and Wenger, *Zeitsch. anal. Chem.*, 1914, 53, 371. Cf. Aloy, *Bull. Soc. chim.*, 1902, [3], 27, 734.

<sup>7</sup> Giolitti, *loc. cit.*

<sup>8</sup> See also Siemssen, *Chem. Zeit.*, 1911, 35, 139, 742.

<sup>9</sup> See Hauser, *Zeitsch. anal. Chem.*, 1908, 47, 677.

<sup>10</sup> For alternative methods for the treatment of ores, see Patera, *Dingl. poly. J.*, 1866, 180, 242; Winkler, *Zeitsch. anal. Chem.*, 1869, 8, 357; Bornträger, *ibid.*, 1895, 34, 437; Glaser, *Chem. Zeit.*, 1912, 36, 1166; Schoel, *J. Ind. Eng. Chem.*, 1919, 11, 842; Scott, *ibid.*, 1922, 14, 531; Brinton and Ellestad, *J. Amer. Chem. Soc.*, 1923, 45, 395; Riss, *Chem. Zeit.*, 1923, 47, 765. For the estimation of uranium in steels and in ferroureum, see König, *Chem. Zeit.*, 1913, 37, 1106; *J. Chem. Soc.*, 1913, 104, A, ii., 985; Kelley, Meyers, and Illingworth, *J. Ind. Eng. Chem.*, 1919, 11, 316.

**Electrolysis.**—Uranium salts in solution in acetic acid may be quantitatively separated by electrolytic means. The uranium is completely precipitated at the anode as hydrated oxide, and this may be converted by ignition to urano-uranic oxide, and weighed as such.<sup>1</sup> A rotating anode should be used.

**Volumetric Methods** for estimating uranium are less satisfactory than those described above. The usual course is to reduce the uranium to the uranous condition by means of zinc and sulphuric acid, and then to titrate the solution with a standard solution of permanganate.<sup>2</sup> The uranium is re-oxidised according to the equation :



According to Pierlé<sup>3</sup> the method is inaccurate owing to the uranium being reduced beyond the uranous condition, and it does not appear possible to eliminate this error, or to take the reduction to any further definite point. The reduction is less satisfactory in hydrochloric acid solution, or by means of stannous chloride. Rapid reduction may be obtained by shaking with zinc amalgam.<sup>4</sup> The end point in the titration may be observed directly, as the green solution gradually becomes yellow and finally assumes a pink tinge; or the process may be followed electrometrically.<sup>5</sup> Methods of titration involving the use of dichromate<sup>6</sup> and of potassium iodide<sup>7</sup> have been described.

A **colorimetric method** of estimating small quantities of uranium in solution depends upon the red colour obtained when a uranyl salt is treated with sodium salicylate.<sup>8</sup> Free mineral acid, iron, acetic acid, alcohol, or acetone must be absent, but neutral alkali salts do not interfere.

The frequent occurrence of vanadium in uranium minerals renders the separation of these two metals of importance. One method in use is based on the solubility of uranyl nitrate in ether,<sup>9</sup> whilst vanadic and also molybdic and tungstic acids are insoluble. A solution containing these substances may therefore be evaporated to dryness, and the uranyl salt extracted from the residue with ether. Another method depends upon the fact that uranyl nitrate is readily soluble, whilst vanadium compounds are insoluble, in acetic acid of 95 per cent. strength to which nitric acid has been added in the proportion 1 : 20.<sup>10</sup>

<sup>1</sup> Smith and Wallace, *J. Amer. Chem. Soc.*, 1898, 20, 279; *Zeitsch. Elektrochem.*, 1898, 8, 167; Kollock and Smith, *J. Amer. Chem. Soc.*, 1901, 23, 607; Wherry and Smith, *ibid.*, 1907, 29, 806; Fischer and Rideal, *Zeitsch. anorg. Chem.*, 1913, 81, 170.

<sup>2</sup> Pulman, *Amer. J. Sci.*, 1903, [4], 16, 229; Kern, *J. Amer. Chem. Soc.*, 1901, 23, 685; Hillebrand, *U.S. Geological Survey*, 1889, 78, 90. See also Newton and Hughes, *J. Amer. Chem. Soc.*, 1915, 37, 1711.

<sup>3</sup> Pierlé, *J. Ind. Eng. Chem.*, 1920, 12, 60.

<sup>4</sup> Ibbotson and Clarke, *Chem. News*, 1911, 103, 146; Nakazono, *J. Chem. Soc. Japan*, 1921, 42, 761; Kikuchi, *ibid.*, 1922, 43, 544; Kanô, *ibid.*, 1922, 43, 550.

<sup>5</sup> Ewing and Eldridge, *J. Amer. Chem. Soc.*, 1922, 44, 1484; Gustavson and Knudson, *ibid.*, 1922, 44, 2756; Kanô, *loc. cit.*

<sup>6</sup> Ewing and Eldridge, *loc. cit.*

<sup>7</sup> Glassmann, *Ber.*, 1904, 37, 189.

<sup>8</sup> Müller, *Chem. Zeit.*, 1919, 43, 739.

<sup>9</sup> Péligot, *Ann. Chim. Phys.*, 1842, [3], 5, 1.

<sup>10</sup> Pierlé, *loc. cit.* See also Finn, *J. Amer. Chem. Soc.*, 1906, 28, 1443; Campbell and Griffin, *J. Ind. Eng. Chem.*, 1909, 1, 661; Moore and Kithil, "A Preliminary Report on Uranium, Radium, and Vanadium," Washington, 1913, *Bureau of Mines Dept. of the Interior Bulletin*, 70; Turner, *Amer. J. Sci.*, 1916, [4], 42, 109.

## CHAPTER X.

### THE RADIOACTIVITY OF URANIUM.

THE radioactivity of uranium <sup>1</sup> was first observed in 1896 by Becquerel,<sup>2</sup> who wrapped a photographic plate in thick black paper and placed upon it a paper containing potassium uranyl sulphate; the whole was exposed to sunlight for several hours, and on development of the plate a black silhouette of the substance was obtained. That the effect was not due to fluorescence was shown by the fact that uranous salts which did not fluoresce were similarly active; nor was exposure to light necessary, for crystals of such salts which had been deposited in the dark and had never been exposed to light produced the same results. The radiations emitted resembled the X-rays discovered by Röntgen in the previous year; they were able to penetrate solid matter, to ionise gases, and to produce fluorescence in certain substances, such as zinc sulphide. They differed, however, in being emitted spontaneously and being unaffected by changes of temperature or of other conditions. It has been observed, for example, that the activity of uranium is the same at 1000° C. as at ordinary temperatures.<sup>3</sup> The property is possessed by all uranium compounds, and the activity remains undiminished after long periods.<sup>4</sup> It is not appreciably affected by exposure to cathode rays.<sup>5</sup> The metal is more strongly active than any of its preparations, whilst naturally occurring ores of uranium are even more active than the pure metal itself, owing to the presence of small quantities of the more highly radioactive element, radium.<sup>6</sup> Indeed, it was this remarkable fact that led to the search for and discovery of radium.

The radioactivity is due to a property possessed by the atoms of the element of undergoing spontaneous degradation with the emission of radiations. The latter may be of three types:  $\alpha$ -rays, consisting of positively charged particles of helium <sup>7</sup> or helium nuclei containing four positive units and two negative—that is in effect, an algebraic total of two positive charges;  $\beta$ -rays, consisting of negative electrons; and

<sup>1</sup> The phenomenon of radioactivity is more fully discussed in Vol. III., Part I., of this series.

<sup>2</sup> Becquerel, *Compt. rend.*, 1896, 122, 420, 501, 559, 689, 762, 1086.

<sup>3</sup> Forsyth, *Phil. Mag.*, 1909, [6], 18, 207.

<sup>4</sup> Becquerel, *Compt. rend.*, 1899, 128, 771. Compare Staehling, *ibid.*, 1919, 169, 1036; 1921, 173, 1468.

<sup>5</sup> Jorissen and Vollgraff, *Chem. Weekblad*, 1914, 11, 832. Compare Jorissen and Ringer, *ibid.*, 1907, 4, 242; Olie, *ibid.*, 1909, 6, 683; La Rosa, *Nuovo Cim.*, 1913, [6], 5, i., 73.

<sup>6</sup> M. and Mme. Curie, *Compt. rend.*, 1898, 127, 175; M. and Mme. Curie, and Bémont, *ibid.*, 1898, 127, 1215. See also McCoy and Ross, *J. Amer. Chem. Soc.*, 1907, 29, 1698.

<sup>7</sup> The actual production of gaseous helium from uranium has been observed. See Soddy, *Nature*, 1908, 79, 129; *Le Radium*, 1908, 5, 361; *Physikal. Zeitsch.*, 1909, 10, 41.

$\gamma$ -rays, similar to X-rays but more penetrating, which generally accompany the emission of  $\beta$ -rays.<sup>1</sup> By the expulsion of an  $\alpha$ -ray the mass of the atom must be decreased by four units, so that an element of lower atomic weight will remain, but one with two positive charges of electricity fewer, and thus in general occupying a position in the Periodic Table two vertical columns to the left of that occupied by the original element. Emission of  $\beta$ - and  $\gamma$ -rays must result in a change in the energy content of the atom, so that again a new element is produced, although of the same atomic weight as the old.

These new elements may themselves be radioactive, and produce in their turn other new elements, so that if a preparation containing a radioactive element, such as uranium, be left untouched for some time, there will be present not only uranium but a number of its disintegration products as well.

The rate at which one substance is produced from another depends upon the rate at which the parent substance emits  $\alpha$ - or  $\beta$ -particles. The time taken for the mass of a radioactive element to be reduced to half its original value is called the "period of half-change" of the element. This varies greatly with different elements, but it is a useful factor, since it bears a constant relation to the fraction disintegrating in unit time. This is expressed by the equation

$$P = \frac{0.6930}{\lambda},$$

where  $P$  is the period of half-change and  $\lambda$  is the radioactive constant, or fraction disintegrating in unit time.

It is clear from the above relation that the radioactive elements with long periods will change only slowly, emitting comparatively few rays, whilst a similar quantity of a short-period element will emit rays much more rapidly. Moreover  $\alpha$ -particles emitted from elements of short life travel with a higher velocity and are consequently of greater range than  $\alpha$ -particles from elements of longer life.

A radioactive substance may also be distinguished by its "average life," *i.e.* the average of the periods during which all the atoms of the element survive before undergoing disintegration. It is denoted by  $L$  and is the reciprocal of the constant  $\lambda$ , and thus equals  $1.443 P$ .

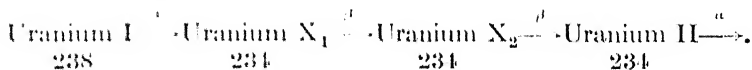
**The Uranium Series.**—Ordinary uranium preparations emit  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays. The  $\alpha$ -rays alone come from the element uranium, the  $\beta$ - and  $\gamma$ -rays coming from products of its disintegration. By expulsion of one  $\alpha$ -particle, the atom of uranium, of atomic weight 238, produces an atom of a new element, known as uranium  $X_1$ , of atomic weight 234. This new atom is more unstable than the original uranium atom and emits a  $\beta$ -particle, producing an atom of another new element, known as uranium  $X_2$ , of the same atomic weight as uranium  $X_1$ .

It was observed by Boltwood<sup>2</sup> in comparing the ionising power of uranium, deprived as far as possible of all its disintegration products, with the ionising power of the other  $\alpha$ -radiating members of the series, that the uranium expelled twice the number of  $\alpha$ -particles given out by any of the other members in equilibrium with it. This was confirmed by

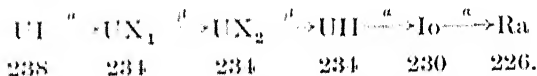
<sup>1</sup> For a full account of the properties of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays, see this series, Vol. III., Part I., pp. 277–282.

<sup>2</sup> Boltwood, *Amer. J. Sci.*, 1908, [4], 25, 269.

direct enumeration of the  $\alpha$ -particles by the scintillation method,<sup>1</sup> and determinations of the range suggested that  $\alpha$ -particles of two slightly differing ranges were being emitted, one of range 2.5 cm. at 15° C. and the other 2.9 cm. Thus the presence in uranium of two different elements, each emitting  $\alpha$ -particles, was indicated. These are probably isotopic, since they appear to possess identical chemical properties and cannot as yet be separated. Their atomic weights should, however, differ by four units: the first, of atomic weight 238, is known as uranium I; the second, of atomic weight 234, as uranium II (see pp. 285, 348). The latter is produced from uranium  $X_2$  by expulsion of a  $\beta$ -particle. We thus have the following scheme:



It has already been observed (pp. 277, 341) that radium occurs in practically all uranium minerals, and it was early suggested that radium was a disintegration product of uranium. This contention was supported by the fact that in old unaltered minerals the ratio of radium to uranium is practically constant, being  $3.40 \pm 0.03 \times 10^{-7}$  on the International Radium Standard.<sup>2</sup> The constancy of this ratio is assumed to be due to radioactive equilibrium being attained between the uranium and its products. Under such conditions the amounts of a parent substance and its successive products present together are inversely proportional to the respective rates of change.<sup>3</sup> The amount of radium present is thus governed by its relative rates of formation and degradation, so that the ratio, radium:uranium, will be constant when the speeds of the opposing reactions are balanced. Soddy observed that radium gradually appeared in a carefully purified solution of uranium nitrate freed from uranium X, but only very slowly, and concluded that an unknown intermediate product of slow transformation occurred between uranium II and radium. Boltwood, in 1907, showed that this intermediate product, which he called ionium, could be isolated. We now have the genetic connection between uranium and radium as follows:<sup>4</sup>



In addition to radium, a constant constituent of uranium minerals, in quantity proportional to the uranium present, is actinium. It does not seem likely, however, that this element can be placed in the direct

<sup>1</sup> Geiger and Rutherford, *Phil. Mag.*, 1910, [6], 20, 691; *Le Radium*, 1910, 7, 225; Brown, *Proc. Roy. Soc.*, 1910, 84, [A], 151; Foch, *Le Radium*, 1911, 8, 101; Geiger and Nuttall, *Phil. Mag.*, 1912, [6], 23, 439.

<sup>2</sup> Lind and Roberts, *J. Amer. Chem. Soc.*, 1920, 42, 1170; Becker and Jannasch, *Jahrb. Radioakt. Elektr.*, 1915, 12, 1. See also Lind and Whittemore, *ibid.*, 1914, 36, 2066; Rutherford, *Phil. Mag.*, 1914, [6], 28, 320; Soddy, *ibid.*, 1908, [6], 16, 632; Heilmann and Marckwald, *Physikal. Zeitsch.*, 1913, 14, 303; Gleditsch, *Le Radium*, 1911, 8, 236; Marckwald and Russell, *Ber.*, 1911, 44, 771; Boltwood, *Amer. J. Sci.*, 1908, [4], 25, 269; 1904, [1], 18, 97; Rutherford and Boltwood, *ibid.*, 1906, [4], 22, 1; 1905, [4], 20, 35. On the relation between uranium and radium, see also Levin, *Physikal. Zeitsch.*, 1907, 8, 802; Soddy and Mackenzie, *Phil. Mag.*, 1907, [6], 14, 272; Soddy and Hitchins, *ibid.*, 1915, [6], 30, 209; Soddy, *ibid.*, 1919, [6], 38, 483.

<sup>3</sup> See this series, Vol. III., Part I., p. 284.

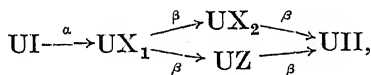
<sup>4</sup> Gohring, *Jahrb. Min.*, 1915, ii., ref. 15. Cf. *Annual Reports Chemical Society*, 1913, 10, 266.

line of descent from uranium through radium. In order to account for its presence as a product of uranium, it must be assumed that there is a branching in the disintegration series, one branch giving radium and its products, the other actinium and its products.

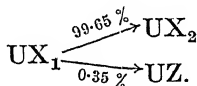
In 1911 Antonoff observed that uranium  $X_1$  shows at first a rapidly falling soft  $\beta$ -ray activity, and attributed the effect to a new radioactive element which he named uranium Y.<sup>1</sup> The existence of this element now appears to be definitely established.<sup>2</sup> It is apparently formed by an  $\alpha$ -ray change from uranium I or uranium II, the latter being the parent more generally accepted.<sup>3</sup> According to this view, uranium II breaks up in two ways, both by expulsion of  $\alpha$ -particles, in the one case producing ionium and in the other uranium Y. The fraction of the uranium II breaking up to form uranium Y is about 3 per cent.

Uranium Y is isotopic with uranium  $X_1$ , and is therefore tetravalent. Since it gives off  $\beta$ -rays, it is unlikely, according to the Group-displacement Law, that it will change directly into trivalent actinium; there should be an intermediate  $\alpha$ -ray product. This conclusion was confirmed by the discovery of eka-tantalum or protoactinium, which is the immediate parent of actinium.<sup>4</sup>

Still another element, to which the name uranium Z has been given, has been found in ordinary uranium salts.<sup>5</sup> Its parent has not been established, but it appears to be either uranium  $X_1$  or an unknown isotope of uranium  $X_1$  of similar period. On the assumption that it comes from uranium  $X_1$  Hahn suggests<sup>6</sup> the following scheme :



and from an observation of the relative activities, concludes that the branching relationship is about 0.35 per cent., thus :



Other products of the disintegration of uranium, notably uranium V<sup>7</sup> and radiouranium,<sup>8</sup> have been described, but their existence has not

<sup>1</sup> Antonoff, *Phil. Mag.*, 1911, [6], 22, 419; 1913, [6], 26, 1058. See also Johnstone and Boltwood, *ibid.*, 1920, [6], 40, 50; *Amer. J. Sci.*, 1920, 50, 1; Antonoff, *Le Radium*, 1913, ro, 406.

<sup>2</sup> Soddy, *Phil. Mag.*, 1914, [6], 27, 215; Hahn and Meitner, *Physikal. Zeitsch.*, 1914, 15, 236. Cf. Fleck, *Phil. Mag.*, 1913, [6], 25, 710; Antonoff, *ibid.*, 1913, [6], 26, 332.

<sup>3</sup> Kirsch, *Sitzungsber. K. Akad. Wiss. Wien*, 1920, 129, [2a], 309; Hahn and Meitner, *Physikal. Zeitsch.*, 1919, 20, 529; Widdowson and Russell, *Phil. Mag.*, 1923, [6], 46, 915; Guy and Russell, *Trans. Chem. Soc.*, 1923, 123, 2618.

<sup>4</sup> Soddy, Cranston, and Hitchins, *Proc. Roy. Soc.*, 1918, 94, [A], 384; *Nature*, 1918, 100, 498; Hahn and Meitner, *Physikal. Zeitsch.*, 1918, 19, 208; 1919, 20, 127, 529; 1920, 21, 591; *Naturwiss.*, 1919, 7, 611; *Ber.*, 1919, 52, [B], 1812; 1921, 54, [B], 69; *Zeitsch. Physik*, 1922, 8, 202. See also Göhring, *Physikal. Zeitsch.*, 1914, 15, 1642. The Actinium Series is described in this series, Vol. IV.

<sup>5</sup> Hahn, *Ber.*, 1921, 54, [B], 1131; *Naturwiss.*, 1921, 9, 84, 236; *Chem. Zentr.*, 1921, i., 1015. See Neuburger, *Naturwiss.*, 1921, 9, 235; *Chem. Zentr.*, 1921, i., 1015.

<sup>6</sup> Hahn, *Zeitsch. physikal. Chem.*, 1923, 103, 461. See also Guy and Russell, *loc. cit.*

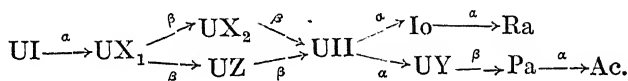
<sup>7</sup> Piccard and Stahel, *Physikal. Zeitsch.*, 1922, 23, 1. Cf. Hahn, *ibid.*, 1922, 23, 146.

<sup>8</sup> Danne, *Compt. rend.*, 1909, 148, 337; *Le Radium*, 1909, 6, 42. See Lloyd, *J. Physical Chem.*, 1910, 14, 509; Sirk, *Monatsh.*, 1912, 33, 289.

been established. Hahn has even suggested the possible existence of an independent radioactive series derived from an unknown uranium isotope, uranium III.<sup>1</sup> Such views, however, have received no experimental confirmation.

It has been observed that the element lead occurs in unaltered primary uranium minerals in amounts proportional to the amount of uranium present.<sup>2</sup> It is not radioactive, but its atomic weight differs from that of ordinary lead, being very little more than 206. It is regarded as highly probable that this element is the end-product of the radium series,<sup>3</sup> so that like radium and actinium it is derived from uranium. It is an isotope of lead, with which it is therefore chemically identical, and is known as Radium G. It is often referred to as *uranium lead*.<sup>4</sup>

The following scheme represents the uranium disintegration series according to the present state of knowledge :



The positions of these elements in the Periodic Table, according to the Group-displacement Law, is shown in the following table :

Group . . .	IIA.	IIIA.	IVA.	VA.	VIa.
Type element .	Ra	Ac	Th	Pa	U
Atomic number .	88	89	90	91	92

#### THE DISINTEGRATION PRODUCTS OF URANIUM AND THEIR SEPARATION.

**Uranium I** is the primary radioactive element. It emits  $\alpha$ -rays and produces uranium  $X_1$ . By counting the number of  $\alpha$ -particles per

<sup>1</sup> See also Neuburger, *loc. cit.*; Piccard, *Arch. Sci. phys. nat. de Genève*, 1917, 44, 161; Johnstone and Boltwood, *Phil. Mag.*, 1920, [6], 40, 66; Joly, *Nature*, 1922, 109, 480; Guy and Russell, *loc. cit.*

<sup>2</sup> Boltwood, *Amer. J. Sci.*, 1907, [4], 23, 77.

<sup>3</sup> See this series, Vol. III., Part I., p. 299.

<sup>4</sup> See Hönigschmid and Birckenbach, *Ber.*, 1923, 56, [B], 1837; Hönigschmid and Steinheil, *ibid.*, p. 1831. For comparison of the band spectra of uranium lead and ordinary lead, see Grebe and Konen, *Physikal. Zeitsch.*, 1921, 22, 546.



gram of uranium, and assuming that half come from uranium I, the period of half-change for this element is found to be approximately  $5 \times 10^9$  years.<sup>1</sup> A similar value may be obtained by comparing the weights of radium and uranium in equilibrium with one another.<sup>2</sup> The most recent value given is  $4.67 \times 10^9$  years.<sup>3</sup> Its average life<sup>4</sup> is  $6.5 \times 10^9$  years.<sup>5</sup> The  $\alpha$ -particles emitted have a velocity of  $1.37 \times 10^9$  cm. per second, and a range at  $15^\circ$  C. of 2.50 cm.;<sup>5</sup> at  $0^\circ$  C. the range is 2.37 cm.<sup>6</sup>

Uranium  $X_1$  may be obtained from solutions of uranium salts by the addition of excess of ammonium carbonate. The precipitate first formed largely redissolves, but leaves a small insoluble residue which contains the  $\beta$ - and  $\gamma$ -activity.<sup>7</sup> The separation is helped by the presence of iron. The uranium  $X_1$  may also be precipitated along with barium sulphate;<sup>8</sup> or it may be obtained by extracting uranium salt solutions with ether or other organic solvents, the uranium  $X_1$  remaining in the aqueous layer.<sup>9</sup> By repeated crystallisation of uranyl or uranous nitrate from aqueous solution the uranium  $X_1$  can be concentrated in the mother-liquor.<sup>10</sup> If this liquor is then treated with ferric chloride in the proportion of 50 milligrams to 100 grams of uranous nitrate, and the iron separated from the diluted solution by carefully warming with ammonium hydroxide and ammonium carbonate, the uranium  $X_1$  is adsorbed by the iron if no weighable quantity of thorium be present.<sup>11</sup> It may be freed from uranium by redissolving, and reprecipitating with ammonia and ammonium carbonate.

It may also be separated from solutions of uranium salts by the addition of a little cerium salt and precipitation with aqueous hydrofluoric acid,<sup>12</sup> or with oxalic acid; or by adding a small quantity of thorium nitrate and precipitating with *m*-nitrobenzoic acid.<sup>13</sup> It may also be absorbed by charcoal,<sup>14</sup> basic ferric acetate,<sup>15</sup> and by various oxides, sulphides, sulphates, and gelatinous silica.<sup>16</sup> In the case of charcoal the uranium  $X_1$  is completely removed from a solution of a

<sup>1</sup> Geiger and Rutherford, *Phil. Mag.*, 1910, [6], 20, 691; *Le Radium*, 1910, 7, 225. See also Meyer, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, 122, [2a], 1085.

<sup>2</sup> Geiger and Nuttall, *Phil. Mag.*, 1912, [6], 23, 439. See also McCoy, *Phys. Review*, 1913, 1, 401.

<sup>3</sup> See International Committee on Chemical Elements, *J. Amer. Chem. Soc.*, 1923, 45, 867.

<sup>4</sup> See this series, Vol. III., Part I., p. 282.

<sup>5</sup> Meyer, *Jahrb. Radioakt. Elektron.*, 1920, 17, 80.

<sup>6</sup> International Committee, *loc. cit.*

<sup>7</sup> Crookes, *Proc. Roy. Soc.*, 1900, 66, 409. See also Soddy, *Phil. Mag.*, 1909, [6], 18, 861.

<sup>8</sup> Becquerel, *Compt. rend.*, 1900, 131, 137; 1901, 133, 977; Soddy, *Trans. Chem. Soc.*, 1902, 81, 860; Berry, *ibid.*, 1910, 97, 196; Soddy and Russell, *Phil. Mag.*, 1909, [6], 18, 620; Schmidt, *Physikal. Zeitsch.*, 1909, 10, 6; Antonoff, *Phil. Mag.*, 1911, [6], 22, 419.

<sup>9</sup> Lloyd, *J. Physical Chem.*, 1910, 14, 509; Moore and Schlundt, *Phil. Mag.*, 1906, [6], 12, 393; Godlewski, *ibid.*, 1905, [6], 10, 45.

<sup>10</sup> Soddy and Russell, *loc. cit.*; Godlewski, *loc. cit.*

<sup>11</sup> Hahn, *Ber.*, 1921, 54, [B], 1134; Meyer and von Schweidler, *Jahrb. Radioakt. Electron.*, 1909, 6, 390.

<sup>12</sup> Keetman, *Jahrb. Radioakt. Elektron.*, 1909, 6, 268.

<sup>13</sup> Guy and Russell, *Trans. Chem. Soc.*, 1923, 123, 2618.

<sup>14</sup> Becquerel, *Compt. rend.*, 1905, 141, 87; Ritzel, *Zeitsch. physikal. Chem.*, 1909, 67, 724; Freundlich and Kaempfer, *ibid.*, 1915, 90, 681; Freundlich, Neumann, and Kaempfer, *Physikal. Zeitsch.*, 1914, 15, 537; Levin, *ibid.*, 1906, 7, 692; *Chem. Zentr.*, 1906, ii., 1757.

<sup>15</sup> Brown, *Trans. Chem. Soc.*, 1922, 121, 1736; Szilárd, *Compt. rend.*, 1909, 149, 113.

<sup>16</sup> Wojtaszewski, *Le Radium*, 1913, 10, 363 (Abs.).

uranium salt by adsorption, but if a small quantity of a thorium salt is added, the uranium  $X_1$  is not adsorbed.<sup>1</sup> This displacement of the adsorption appears to be due to the presence of colloidal particles in the thorium nitrate, for if these particles are removed by previously shaking with charcoal, or by dialysis, or cataphoresis, the thorium nitrate is no longer able to prevent the adsorption.

Electrochemical methods of separation are not practicable.<sup>2</sup>

The period of half-change of uranium  $X_1$  is  $23.82 \pm 0.075$  days.<sup>3</sup> It emits soft  $\beta$ -rays,<sup>4</sup> so soft that they were at first taken for  $\alpha$ -rays.<sup>5</sup> A hard  $\beta$ -radiation ascribed to it was afterwards found to be due to uranium  $X_2$ .<sup>6</sup> It also gives very weak  $\gamma$ -rays.<sup>7</sup>

Diffusion experiments in solution show that uranium  $X_1$  is tetravalent.<sup>8</sup> It is isotopic with thorium<sup>9</sup> and ionium,<sup>10</sup> and therefore has the same chemical properties.

**Uranium  $X_2$ , or Brevium,**<sup>11</sup> is deposited on lead by electrochemical action, either by immersing a lead plate in a concentrated solution of uranium  $X_1$ , or by shaking an acid solution of iron containing uranium  $X_1$  in a clean lead crucible and then removing the liquid.<sup>12</sup> The lead shows a very penetrating  $\beta$ -activity, which at first falls very rapidly in value. The uranium  $X_2$  is also deposited, but in smaller quantity, on zinc or magnesium.<sup>13</sup> It may be separated quantitatively from uranium  $X_1$  by precipitating along with bismuth oxychloride,<sup>13</sup> or by filtering a solution of uranium X in fairly strong acid through a filter paper on which tantalum pentoxide has been previously filtered. In this way uranium  $X_2$  is held back and freed from all but about 1 per cent. of uranium  $X_1$ .<sup>14</sup>

Uranium  $X_2$ , the product of uranium  $X_1$ , has a period of half-change of only 1.15 minutes.<sup>15</sup> It emits both  $\beta$ - and  $\gamma$ -rays,<sup>16</sup> the former prob-

<sup>1</sup> Freundlich and Wreschner, *Zeitsch. physikal. Chem.*, 1923, 106, 366.

<sup>2</sup> Rossi, *Nuovo Cim.*, 1913, [6], 5, i., 5; von Sensel, *Zeitsch. physikal. Chem.*, 1910, 71, 563.

<sup>3</sup> Kirsch, *Sitzungsber. K. Akad. Wiss. Wien*, 1920, 129, 309. See also Rutherford and Soddy, *Phil. Mag.*, 1903, [6], 5, 441; Soddy and Russell, *ibid.*, 1910, [6], 19, 847.

<sup>4</sup> Soddy, *Trans. Chem. Soc.*, 1902, 81, 860; *Nature*, 1909, 80, 37; *Phil. Mag.*, 1909, [6], 18, 858; Rutherford and Grier, *Phil. Mag.*, 1902, [6], 4, 323; Levin, *Physikal. Zeitsch.*, 1907, 8, 585; 1908, 9, 655; Hahn and Rothenbach, *ibid.*, 1919, 20, 194; Meitner, *Zeitsch. Physik*, 1923, 7, 54.

<sup>5</sup> Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1907, 116, [2a], 109; Levin, *Physikal. Zeitsch.*, 1907, 8, 129.

<sup>6</sup> See Fajans and G6hring, *Physikal. Zeitsch.*, 1913, 14, 877.

<sup>7</sup> Soddy, *Trans. Chem. Soc.*, 1902, 81, 860; *Phil. Mag.*, 1910, [6], 20, 342; Soddy and Russell, *Nature*, 1909, 80, 7; *Physikal. Zeitsch.*, 1909, 10, 249; *Phil. Mag.*, 1909, [6], 18, 620; Eve, *Physikal. Zeitsch.*, 1907, 8, 185; Baeyer, Hahn, and Meitner, *ibid.*, 1914, 15, 649; *Zeitsch. Physik*, 1923, 7, 157; Meitner, *loc. cit.*; Richardson, *Phil. Mag.*, 1914, [6], 27, 252.

<sup>8</sup> von Hevesy, *Physikal. Zeitsch.*, 1913, 14, 49, 1202.

<sup>9</sup> Fleck, *Trans. Chem. Soc.*, 1913, 102, 381.

<sup>10</sup> Soddy, *ibid.*, 1911, 99, 82.

<sup>11</sup> G6hring, *Jahrb. Min.*, 1915, ii., Ref. 15. Cf. *Annual Reports, Chemical Society*, 1913, 10, 266.

<sup>12</sup> Fajans and G6hring, *loc. cit.*; Hahn and Rothenbach, *Physikal. Zeitsch.*, 1919, 20, 196.

<sup>13</sup> Fleck, *Phil. Mag.*, 1913, [6], 26, 528.

<sup>14</sup> Hahn and Meitner, *Physikal. Zeitsch.*, 1913, 14, 758. See also Fajans and G6hring, *loc. cit.*

<sup>15</sup> Fajans and G6hring, *loc. cit.*; Fleck, *loc. cit.*; Hahn and Meitner, *loc. cit.* Guy and Russell give 1.175 minutes (*Trans. Chem. Soc.*, 1923, 123, 2618).

<sup>16</sup> Richardson, *loc. cit.*

ably being more penetrating than those from uranium  $X_1$ . Its position in the Periodic Table, according to the Group-displacement Law, is in Group V., and it shows chemical similarity to both tantalum and bismuth. The iodide is less volatile than bismuth iodide.

**Uranium Z**, also thought to be a product of uranium  $X_1$ , was discovered by Hahn in 1921,<sup>1</sup> who isolated it in the following manner. The mother-liquors from repeated fractional crystallisations of uranic nitrate, containing uranium  $X_1$  and uranium Z, were treated with ferric chloride solution, and the iron precipitated by means of ammonia and ammonium carbonate. The precipitate, which contained both the uranium  $X_1$  and uranium Z, was treated with a solution of tantalum in hydrofluoric acid, lanthanum nitrate added, and the mixture digested on a water-bath with dilute hydrofluoric and sulphuric acids. Lanthanum fluoride was precipitated, and carried down with it uranium  $X_1$ . The filtrate was evaporated to dryness and the residue ignited. The tantalum was thus rendered insoluble, whilst the iron could be removed by means of concentrated hydrochloric acid. The uranium Z remained with the tantalum. By this means Hahn obtained specimens of uranium Z which were 99.5 per cent. radioactively pure.

Uranium Z is isotopic with protoactinium, and has a period of half-change of 6.7 hours.<sup>2</sup> It emits a highly complex  $\beta$ -radiation, of which the intensity, however, is only 0.25 per cent. of that of uranium ( $X_1 + X_2$ ). The fraction of uranium forming uranium Z is only about 0.35 per cent.<sup>3</sup>

**Uranium II**, the product of uranium  $X_2$  and probably also of uranium Z, is considered to be the second  $\alpha$ -ray-producing substance present in uranium, isotopic with uranium I and inseparable from it.<sup>4</sup> The range of its  $\alpha$ -particles is 2.9 cm., and the period of half-change is probably about  $2 \times 10^6$  years.<sup>5</sup> The quantities of the two isotopes present in uranium in the condition of radioactive equilibrium will be proportional to their periods of half-change, so that not more than 0.04 per cent. of uranium II can be present. The atomic weight of uranium is therefore practically identical with that of uranium I (see p. 285). Unsuccessful attempts have been made to separate the two isotopes by diffusion in solution.<sup>6</sup>

**Ionium**, the product of uranium II and the immediate parent of radium, was isolated by Boltwood in 1907.<sup>7</sup>

It may be obtained in quantity by separating and purifying thorium from uranium minerals or residues;<sup>8</sup> the ionium remains with the thorium and cannot be separated from it.

Ionium emits  $\alpha$ -particles of range 3.07 cm. at 15° C. and of initial

<sup>1</sup> Hahn, *Ber.*, 1921, 54, [B], 1131; *Naturwiss.*, 1921, 9, 84, 236. See *Chem. Zentr.*, 1921, i., 1015.

<sup>2</sup> Hahn, *Zeitsch. physikal. Chem.*, 1923, 103, 461; Guy and Russell, *Trans. Chem. Soc.*, 1923, 123, 2618.

<sup>3</sup> Hahn, *loc. cit.*

<sup>4</sup> Fajans and Göhring, *Physikal. Zeitsch.*, 1913, 14, 877.

<sup>5</sup> See Meyer, *Jahrb. Radioakt. Elektron.*, 1920, 17, 80; Geiger and Nuttall, *Phil. Mag.*, 1912, [6], 23, 439.

<sup>6</sup> Lachs, Nadratowska, and Wertenstein, *Compt. rend. Soc. Sci. Warsaw*, 1917, 9, 67; see *J. Chem. Soc.*, 1918, 114, Abs. ii., 213. See also von Hevesy and von Putnoký, *Physikal. Zeitsch.*, 1913, 14, 63; *Phil. Mag.*, 1913, [6], 25, 415.

<sup>7</sup> Boltwood, *Amer. J. Sci.*, 1907, 24, 370; 1908, 25, 365; see also *ibid.*, 1906, 22, 537. Also see Rutherford, *Nature*, 1907, 75, 270; 76, 661; *Phil. Mag.*, 1907, [6], 14, 733.

<sup>8</sup> Boltwood, *loc. cit.*; Hahn, *Ber.*, 1907, 40, 4415; Marckwald and Keetman, *ibid.*, 1908, 41, 49; Keetman, *Jahrb. Radioakt. Elektron.*, 1906, 6, 265. See also Szilárd, *Le Radium*, 1909, 6, 80; Meitner, *Physikal. Zeitsch.*, 1915, 16, 4.

velocity  $1.46 \times 10^9$  cm. per sec.,<sup>1</sup> and also  $\gamma$ -rays.<sup>2</sup> Its period of half-change is  $9 \times 10^4$  years.<sup>3</sup> In accordance with the Group-displacement Law the element should be in Group IVA of the Periodic Table, and therefore isotopic with thorium and uranium  $X_1$  (see table, p. 345). The isotopy with thorium is confirmed by the result of the spectroscopic examination of thorium preparations rich in ionium, which give only the spectrum of thorium.<sup>4</sup> The chemical reactions of ionium are therefore exactly the same as those of thorium.<sup>5</sup> That ionium is tetravalent is shown by diffusion experiments in solution.<sup>6</sup>

Preparations of ionium are used as standards of  $\alpha$ -ray activity when a more active standard than urano-uranic oxide is necessary. The production of helium from ionium has been observed.<sup>7</sup> Uranium  $X_1$  may be used as an indicator for ionium when estimating the latter in terms of the equilibrium quantity contained in uranium minerals.<sup>8</sup>

From the position of ionium in the disintegration series, its atomic weight should be approximately 230. Hönigschmid found<sup>9</sup> 231.5 for thorium-ionium mixtures obtained from minerals poor in thorium.

The product of ionium is radium.<sup>10</sup>

Uranium Y, isotopic with uranium  $X_1$ ,<sup>11</sup> appears, like ionium, to be produced by an  $\alpha$ -ray change from uranium II (see p. 344). It is obtained in the precipitate with uranium  $X_1$  when a solution of uranium nitrate containing iron is treated with ammonia and ammonium carbonate; but after a few days the amount of uranium Y in the solution rises to its maximum value again, whilst very little uranium  $X_1$  is formed, so that by repeating the precipitation, iron containing the maximum quantity of uranium Y with very little uranium  $X_1$  is obtained.<sup>12</sup> The two isotopes are also precipitated together along with cerous fluoride; they can then be removed from the cerium by adding a little zirconium salt and precipitating with sodium hypophosphate,  $\text{NaHPO}_3 \cdot 3\text{H}_2\text{O}$ .<sup>13</sup> Uranium Y emits  $\beta$ -rays and has a period of half-change of 27.5 hours.<sup>14</sup> The fraction of the uranium breaking up to form uranium Y is about 3 per cent.<sup>15</sup>

Protoactinium, or eka-tantalum, the product of uranium Y, was

<sup>1</sup> Geiger and Nuttall, *Phil. Mag.*, 1911, [6], 22, 613. See Meyer, *Jahrb. Radioakt. Elektron.*, 1920, 17, 80.

<sup>2</sup> Meyer, *loc. cit.*

<sup>3</sup> Soddy, *Le Radium*, 1910, 7, 295; *Nature*, 1912, 89, 203; *Phil. Mag.*, 1919, [6], 38, 483; Soddy and Hitchens, *Phil. Mag.*, 1915, [6], 30, 209; Piutti, *Le Radium*, 1911, 8, 204; Russell and Rossi, *Proc. Roy. Soc.*, 1912, 87, [A], 478; Meyer, *Jahrb. Radioakt. Elektron.*, 1920, 17, 80; *Monatsh.*, 1916, 37, 347. The International Committee on Chemical Elements (*J. Amer. Chem. Soc.*, 1923, 45, 867) give  $6.9 \times 10^4$  years.

<sup>4</sup> Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, 121, [2a], 1075; Russell and Rossi, *loc. cit.*

<sup>5</sup> See this series, Vol. V.

<sup>6</sup> von Hevesy, *Physikal. Zeitsch.*, 1913, 14, 49.

<sup>7</sup> Boltwood, *Le Radium*, 1911, 8, 104; *Proc. Roy. Soc.*, 1911, 85, [A], 77.

<sup>8</sup> Rona, *Ber.*, 1922, 55, [B], 294.

<sup>9</sup> Hönigschmid, *Zeitsch. Elektrochem.*, 1916, 22, 18; Hönigschmid and Horowitz, *Monatsh.*, 1916, 37, 335.

<sup>10</sup> The radioactive properties of radium are described in Vol. III., Part I., of this series.

<sup>11</sup> See Soddy, *Phil. Mag.*, 1914, [6], 27, 215. <sup>12</sup> Antonoff, *Le Radium*, 1913, 10, 406.

<sup>13</sup> Kirsch, *Sitzungsber. K. Akad. Wiss. Wien*, 1920, 129, [2a], 309.

<sup>14</sup> Guy and Russell, *Trans. Chem. Soc.*, 1923, 123, 2618. Somewhat different values are given by Antonoff, *loc. cit.*; *Phil. Mag.*, 1911, [6], 22, 419; 1913, [6], 26, 1058; Kirsch, *loc. cit.*; Johnstone and Boltwood, *Phil. Mag.*, 1920, [6], 40, 50; *Amer. J. Sci.*, 1920, 50, 1; Hahn and Meitner, *Physikal. Zeitsch.*, 1914, 15, 236; *Naturwiss.*, 1919, 7, 611; *Ber.*, 1919, 52, [B], 1812; *Zeitsch. Physik.*, 1922, 8, 202.

<sup>15</sup> Kirsch, *loc. cit.*; Hahn and Meitner, *Physikal. Zeitsch.*, 1919, 20, 529; Widdowson and Russell, *Phil. Mag.*, 1923, [6], 46, 915; Guy and Russell, *loc. cit.*

discovered independently by Hahn<sup>1</sup> and by Soddy<sup>2</sup> in 1917. It is the parent of actinium,<sup>3</sup> but appears to be genetically connected with uranium. In old minerals the ratio, uranium : actinium, is constant,<sup>4</sup> but the amount of actinium present is less than would be expected if it were a direct disintegration product of uranium. It is therefore thought to lie in a side-chain, and its relation to uranium depends upon which isotope is considered to be the parent of uranium Y. In any case, by the Group-displacement Law protoactinium should be an element in Group VA, and therefore similar to tantalum. It was this consideration which led to its discovery. Hahn added a little potassium tantalum fluoride to a large quantity of pitchblende residues after treatment with hot concentrated nitric acid. He extracted with hydrofluoric acid, evaporated the solution with sulphuric acid, and added concentrated nitric acid to the residue, most of which dissolved. The undissolved part was found to emit  $\alpha$ -rays of low range and to produce actinium. Soddy obtained a sublimate, similarly active, by heating pitchblende in carbon tetrachloride vapour under conditions in which tantalum pentoxide was volatilised.

The following method may be used for the extraction of protoactinium from residues of uranium minerals. After prolonged boiling with nitric acid, which dissolves most of the radioactive constituents present, including radium, small quantities of thorium and lead nitrates and of tantalum oxide are added to the undissolved portion. Upon extracting with hydrofluoric and sulphuric acids the tantalum and protoactinium go into solution. This solution is evaporated and the residue ignited. Any iron, zirconium, etc., may be removed by boiling with aqua regia; the tantalum and protoactinium remain insoluble. No method is yet known for the separation of these two elements.

The period of half-change is about 12,000 years.<sup>5</sup>

The atomic weight of protoactinium is important since upon its value all the atomic weights of the actinium series depend. If uranium Y has atomic weight 230, as is the case if uranium II is the parent of uranium Y, that of protoactinium is also 230, and this is the generally accepted value. If, however, uranium I should be the parent of uranium Y, the atomic weight of protoactinium must be 234, and the generally accepted atomic weights of the actinium series would all have to be increased by 4 units.<sup>6</sup>

The properties of the elements of the uranium disintegration series are summarised in the accompanying table.

<sup>1</sup> Hahn and Meitner, *Physikal. Zeitsch.*, 1918, 19, 208; 1919, 20, 127, 529; 1920, 21, 591; *Naturwiss.*, 1919, 7, 611; *Ber.*, 1919, 52, [B], 1812; 1921, 54, [B], 69; *Zeitsch. Physik*, 1922, 8, 202.

<sup>2</sup> Soddy, Cranston, and Hitchins, *Proc. Roy. Soc.*, 1918, 94, [A], 384; *Nature*, 1918, 100, 498. See also Göhring, *Physikal. Zeitsch.*, 1914, 15, 1642.

<sup>3</sup> The actinium series is described in this series, Vol. IV.

<sup>4</sup> Boltwood, *Phys. Review*, 1906, 22, 320; *Amer. J. Sci.*, 1906, [4], 22, 537; 1908, [4], 25, 269; McCoy, *Phil. Mag.*, 1906, [6], 11, 177; McCoy and Ross, *J. Amer. Chem. Soc.*, 1907, 29, 1698. See also Piccard, *Arch. Sci. phys. nat.*, 1917, [4], 44, 161; Meyer and Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1919, 128, [2a], 909; *Chem. Zentr.*, 1920, iii, 435; Hahn and Meitner, *Zeitsch. Physik*, 1921, 8, 202; Smekal, *Physikal. Zeitsch.*, 1921, 22, 48; Piccard and Stahel, *ibid.*, 1922, 23, 1.

<sup>5</sup> International Committee, *loc. cit.*; Hahn and Meitner, *Ber.*, 1921, 54, [B], 69; Mennie, *Phil. Mag.*, 1923, [6], 46, 675.

<sup>6</sup> Russell, *Nature*, 1923, 111, 703, suggests that the parent of uranium Y is a third isotope of uranium, as yet unknown. See also *Phil. Mag.*, 1923, [6], 46, 642.

# CONSTANTS OF THE URANIUM SERIES.<sup>1</sup>

## THE RADIOACTIVITY OF URANIUM.

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Element.	Atomic weight.	Period of half-change.		Average life.	Radioactive constant, $\lambda$ .	Radiation.	Velocity of rays, cm. per sec.	Range of $\alpha$ -rays in cm.	
		M.	I.C.					At 0° C. and 760 mm.	At 15° C. and 760 mm.
UI	238.2	$4.5 \times 10^8$ yr.	$4.67 \times 10^8$ yr.	M.	M.	I.C.	M.	I.C.	M.
UX <sub>1</sub>	234	23.8 days	24.6 days	$6.5 \times 10^8$ yr.	$1.54 \times 10^{-10}$ (yr.) <sup>-1</sup>	$\alpha$	$1.37 \times 10^9$	2.37	2.50
UX <sub>2</sub>	234	1.175 min. <sup>2</sup>	1.15 min.	34.4 days	$2.9 \times 10^{-2}$ (days) <sup>-1</sup>	$\beta$	$1.44 \times 10^{10}$ to $1.77 \times 10^{10}$		
UZ	234	6.69 hr. <sup>2</sup>	6-7 hr.	1.66 min.	0.60 (min.) <sup>-1</sup>	$\beta, \gamma$	$2.46 \times 10^{10}$ to $2.88 \times 10^{10}$		
UII	234	$c. 2 \times 10^6$ yr.	$2 \times 10^6$ yr.	..	..	$\beta^2$			
Io	230	$9 \times 10^4$ yr.	$6.9 \times 10^4$ yr.	$3 \times 10^6$ yr.	$c. 3 \times 10^{-7}$ (yr.) <sup>-1</sup>	$\alpha$	$1.44 \times 10^9$	2.75	2.90
Ra	226	$1730$ yr. <sup>3</sup>	1690 yr.	$1.3 \times 10^5$ yr.	$7.7 \times 10^{-6}$ (yr.) <sup>-1</sup>	$\alpha, \gamma$ (M.)	$1.46 \times 10^9$	2.85	3.07
UY	230	24.6 hr.	27.8 hr. <sup>2</sup>	2280 yr.	$4.38 \times 10^{-4}$ (yr.) <sup>-1</sup>	$\alpha, \beta, \gamma$	$\alpha 1.53 \times 10^9$ $\beta 1.56 \times 10^{10}$ to $1.95 \times 10^{10}$	3.13	3.52
Pa	230	..	$1.2 \times 10^4$ yr.	35.5 hr.	$2.82 \times 10^{-2}$ (hr.) <sup>-1</sup>	$\beta$			
Ac	226	..	20 yr.	$1.7 \times 10^5$ yr. (B.)	..	$\alpha$	..	3.314	
				28.8 yr. (I.C.)					

<sup>1</sup> M refers to the table of Radioactive Constants compiled by Meyer, *Jahrb. Radioakt. Elektron.*, 1920, 17, 80; I.C. refers to the tables given by the International Committee on Chemical Elements, see *J. Amer. Chem. Soc.*, 1923, 45, 867; exceptions are indicated by footnotes. See also this series, Vol. III., Part I., Table of Constants of the Uranium-Radium Series.

<sup>2</sup> Guy and Russell, *Trans. Chem. Soc.*, 1923, 123, 123, 2618.

<sup>3</sup> Geiger and Werner, *Zeitsch. Physik*, 1924, 21, 187.

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